

CHAPTER 6: AQUATIC CHEMISTRY

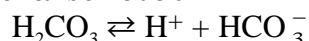
INTRODUCTION

Water continually transforms the surface of the Earth, through interaction with the solid surface and transport of dissolved and suspended matter. Beyond that, water is essential to life and central to human activity. Thus as a society, we are naturally very concerned with water quality, which in essence means water chemistry. Aquatic chemistry is therefore the principal concern of many geochemists.

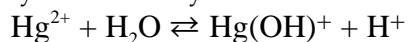
In this chapter, we learn how the tools of thermodynamics and kinetics are applied to water and its dissolved constituents. We develop methods, based on the fundamental thermodynamic tools already introduced, for predicting the species present in water at equilibrium. We then examine the interaction of solutions with solids through precipitation, dissolution, and adsorption.

Most reactions in aqueous solutions can be placed in one of the following categories:

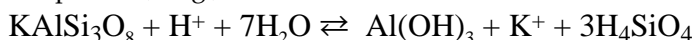
- Acid-base, e.g., dissociation of carbonic acid:



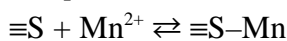
- Complexation, e.g., hydrolysis of mercury:



- Dissolution/Precipitation, e.g., dissolution of orthoclase:



- Adsorption/Desorption, e.g., adsorption of Mn on a clay surface:



(where we are using $\equiv\text{S}$ to indicate the surface of the clay).

In this chapter, we will consider these in detail. We return to the topic of aquatic chemistry in Chapter 13, we examine the weathering process, that is reaction of water and rock and development of soils, and the chemistry of streams and lakes.

ACID-BASE REACTIONS

The hydrogen and hydroxide ions are often participants in all the foregoing reactions. As a result, many of these reactions are pH dependent. In order to characterize the state of an aqueous solution, e.g., to determine how much CaCO_3 a solution will dissolve, the complexation state of metal ions, or the redox state of Mn, the first step is usually to determine pH. On a larger scale, weathering of rock and precipitation of sediments depend critically on pH. Thus pH is sometimes called the *master variable* in aquatic systems. We note in passing that while pH represents the hydrogen ion, or proton concentration, the hydroxide ion concentration is easily calculated from pH since the proton and hydroxide concentrations are related by the dissociation constant for water, i.e., by:

$$K_w = [\text{a}_{\text{H}^+}][\text{a}_{\text{OH}^-}] \quad 6.1$$

The value of K_w , like all equilibrium constants, depends on temperature, but is 10^{-14} at 25°C .

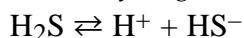
Arrhenius defined an *acid* as a substance that upon solution in water releases free protons. He defined a *base* as a substance that releases hydroxide ions in solution. These are useful definitions in most cases. However, chemists generally prefer the definition of Brønstead, who defined acid and base as proton donors and proton acceptors respectively. The strength of an acid or base is measured by its tendency to donate or accept protons. The dissociation constant for an acid or base is the quantitative measure of this tendency and thus is a good indication of its strength. For example, dissociation of HCl:



CHAPTER 6: AQUATIC CHEMISTRY

has a dissociation constant: $K_{\text{HCl}} = \frac{[\text{H}^+][\text{Cl}^-]}{[\text{HCl}]} = 10^3$

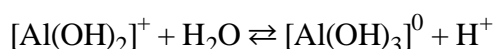
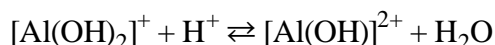
HCl is a strong acid because only about 3% of the HCl molecules added will remain undissociated. The equilibrium constant for dissociation of hydrogen sulfide:



is: $K_{\text{H}_2\text{S}} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} = 10^{-7.1}$

Thus H_2S is a weak acid because very few of the H_2S molecules actually dissociate except at high pH.

Metal hydroxides can either donate or accept protons, depending on pH. For example, we can represent this in the case of aluminum as:



Compounds that can either accept or donate protons are said to be *amphoteric*.

Metals dissolved in water are always surrounded by solvation shells. The positive charges of the hydrogens in the surrounding water molecules are to some extent repelled by the positive charge of the metal ion. For this reason, water molecules in the solvation shell are more likely to dissociate and give up a proton more readily than other water molecules. Thus the concentration of such species will affect pH.

Most protons released by an acid will complex with water molecules to form hydronium ions, H_3O^+ or even $\text{H}_5\text{O}_2^{2+}$. However, in almost all cases we need not concern ourselves with this and can treat the H^+ ion as if it were a free species. Thus we will use $[\text{H}^+]$ to indicate the concentration of $\text{H}^+ + \text{H}_3\text{O}^+ + \text{H}_5\text{O}_2^{2+} + \dots$

PROTON ACCOUNTING, CHARGE BALANCE, AND CONSERVATION EQUATIONS

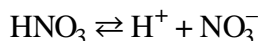
PROTON ACCOUNTING

Knowing the pH of an aqueous system is the key to understanding it and predicting its behavior. This requires a system of accounting for the H^+ and OH^- in the system. There are several approaches to doing this. One such approach is the *Proton Balance Equation* (e.g., Pankow, 1991). In this system, both H^+ and OH^- are considered components of the system, and the proton balance equation is written such that *the concentration of all species whose genesis caused the production of OH^- are written on one side, and the concentration of all species whose genesis caused the production of H^+ are written on the other side*. Because water dissociates to form H^+ and OH^- , $[\text{H}^+]$ always appears on the left side (because one OH^- will have been produced for every H^+ produced by dissociation of water) and OH^- always appears on the right side of the proton balance equation (because one H^+ will have been produced for every OH^- produced). The proton balance equation for pure water is thus:

$$[\text{H}^+] = [\text{OH}^-] \quad 6.2$$

Thus in pure water the concentrations of H^+ and OH^- are equal.

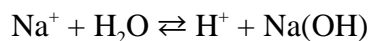
Now, consider the example of a nitric acid solution. H^+ will be generated both by dissociation of water and dissociation of nitric acid:



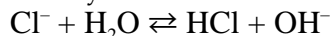
Since one NO_3^- ion is generated for every H^+ , the proton balance equation becomes:

$$[\text{H}^+] = [\text{OH}^-] + [\text{NO}_3^-] \quad 6.3$$

Next consider a solution of sodium chloride. Hydrogen ions may be generated by hydrolysis of sodium:



and hydroxide ions may be generated by:



CHAPTER 6: AQUATIC CHEMISTRY

The proton balance equation for this reaction is:

$$[\text{H}^+] + [\text{HCl}] = [\text{OH}^-] + [\text{NaOH}] \quad 6.4$$

Now consider a solution of a *diprotic* acid such as H_2S . H_2S can undergo 2 dissociation reactions:



For every HS^- ion produced by dissociation of H_2S , one H^+ ion would have been produced. For every S^{2-} ion, however, 2 H^+ would have been produced, one from the first dissociation and one from the second. The proton balance equation is thus:

$$[\text{H}^+] = [\text{OH}^-] + [\text{HS}^-] + 2[\text{S}^{2-}] \quad 6.7$$

An alternative approach to the proton balance equation is the *TOTH proton mole balance equation* used by Morel and Hering (1993). In this system, H^+ and H_2O are always chosen as components of the system but OH^- is not. The species OH^- is the algebraic sum of H_2O less H^+ :

$$\text{OH}^- = \text{H}_2\text{O} - \text{H}^+ \quad 6.8$$

Because aquatic chemistry almost always deals with dilute solutions, the concentration of H_2O may be considered fixed at a mole fraction of 1, or 55.4 M. Thus in the Morel and Hering system, H_2O is made an implicit component, i.e., its presence is assumed by not written, so that equation 6.8 becomes:

$$[\text{OH}^-] = -[\text{H}^+] \quad 6.9$$

The variable *TOTH* is the concentration of the component H^+ , rather than the species H^+ . Because of equation 6.9, *TOTH* for pure water is:

$$\text{TOTH} = [\text{H}^+] - [\text{OH}^-]$$

Thus *TOTH* in this case is the difference between the concentrations of H^+ and OH^- . Now let's consider our example of the NaCl solution. In addition to H^+ and H_2O , we chose Na^+ and Cl^- as components. The species HCl is then produced by combining components H^+ and Cl^- . The species NaOH , however, is:

$$\text{NaOH} = \text{Na}^+ + \text{H}_2\text{O} - \text{H}^+$$

Thus in the proton mole balance equation, HCl counts positively and NaOH negatively:

$$\text{TOTH} = [\text{H}^+] + [\text{HCl}] - [\text{OH}^-] - [\text{NaOH}] \quad 6.10$$

Comparing equations 6.10 and 6.4, we see that the *TOTH* is equal to the difference between the left and right hand sides of the proton balance equation. Alternatively, we may say that *in the TOTH equation, the concentration of all species whose genesis caused the production of OH^- are written as positive, and the concentration of all species whose genesis caused the production of H^+ are written as negative.*

CHARGE BALANCE

As we saw in Chapter 3, solutions are electrically neutral; that is, the number of positive and negative charges must balance:

$$\sum_i m_i z_i = 0 \quad 6.11$$

where m is the number of moles of ionic species i and z is the charge of species i . Equation 6.11 is known as the *charge balance equation* and is identical to equation 3.111. This equation provides an important constraint on the composition of a system. Notice that in some cases, the proton balance and charge balance equations are identical (e.g., equations 6.2 and 6.7).

CONSERVATION EQUATIONS

A further constraint on the composition of a system is provided by *mass balance*. Acid-base reactions will not affect the total concentration of a substance. Thus regardless of reactions 6.5 and 6.6, and any other complexation reactions, such as



CHAPTER 6: AQUATIC CHEMISTRY

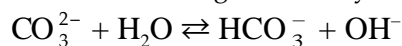
EXAMPLE 6.1. PROTON, MASS, AND CHARGE BALANCE EQUATIONS FOR Na_2CO_3 SOLUTION

Write the proton, proton mass balance, and charge balance, and carbonate conservation equations for a solution prepared by dissolving Na_2CO_3 in water. Assume that Na_2CO_3 dissociates completely and that the system is closed.

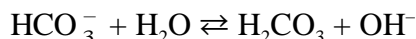
Answer: We begin with the proton balance equation. From the dissociation of water we have:

$$[\text{H}^+] = [\text{OH}^-]$$

In addition to this, hydroxide ions will also be generated by reaction between CO_3^{2-} and water:



and



Since for each HCO_3^- formed, one OH^- must have formed and for each H_2CO_3 present two OH^- must have formed, the proton balance equation is:

$$[\text{H}^+] + [\text{HCO}_3^-] + 2[\text{H}_2\text{CO}_3] = [\text{OH}^-] \quad 6.13$$

Choosing the carbonate and sodium ions as components (in addition to H^+ and H_2O), the bicarbonate and carbonic acid species are combinations of carbonate and one and two, respectively, protons, so that the proton mole balance equation is:

$$\text{TOT H} = [\text{H}^+] + [\text{HCO}_3^-] + 2[\text{H}_2\text{CO}_3] - [\text{OH}^-] \quad 6.14$$

The charge balance equation is:

$$[\text{H}^+] + [\text{Na}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad 6.15$$

The conservation equation for carbonate species is:

$$\Sigma \text{CO}_3 = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3] \quad 6.16$$

Since the dissolution of Na_2CO_3 produces two moles of Na^+ for every mole of carbonate species, we may also write:

$$[\text{Na}^+] = 2\Sigma \text{CO}_3 = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3]$$

the total concentration of sulfide remains constant. Thus we may write:

$$\Sigma \text{S} = [\text{H}_2\text{S}] + [\text{HS}^-] + [\text{S}^{2-}] + [\text{PbS}] + \dots \quad 6.17$$

We can write one mass balance, or *conservation*, equation for each component in solution. Of course for components, such as Na, that form only one species, Na^+ in this case, the mass balance equation is trivial. Mass balance equations are useful for those components forming more than one species.

While the charge balance constraint is an absolute one and always holds, mass balance equations can be trickier because other processes, such as a redox, precipitation, and adsorption, can affect the concentration of a species. We sometimes get around this problem by writing the mass balance equation for an element, since an elemental concentration is not changed by redox processes. We might also define our system such that it is closed to get around the other problems. Despite these restrictions, mass balance often provides a useful additional constraint on a system.

For each acid-base reaction an equilibrium constant expression may be written. By manipulating these equilibrium constant expressions as well as proton balance, charge balance, and mass balance equations, it is possible to predict the pH of any solution. In natural systems where there are many species present, however, solving these equations can be a complex task indeed. An important step in their solution is to decide which reactions have an insignificant effect on pH and neglect them.

THE CARBONATE SYSTEM

We now turn our attention to carbonate. Carbonate in its various species, among which we count CO_2 , is extremely important in geochemistry for a variety of reasons, not the least of which is that carbonate is the principal control on the pH of most natural aqueous systems. Water at the surface of the Earth inevitably contains dissolved CO_2 , either as a result of equilibration with the atmosphere or because of respiration by organisms. CO_2 reacts with water to form *carbonic acid*:

CHAPTER 6: AQUATIC CHEMISTRY

Table 6.1. EQUILIBRIUM CONSTANTS FOR THE CARBONATE SYSTEM

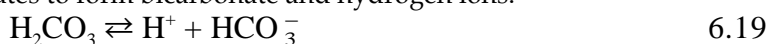
T (°C)	pK _{CO₂}	pK ₁	pK ₂	pK _{cal}	pK _{arag}	K _{CaHCO₃⁺*}	pK _{CaCO₃⁺†}
0	1.11	6.58	10.63	8.38	8.22	-0.82	-3.13
5	1.19	6.52	10.55	8.39	8.24	-0.90	-3.13
10	1.27	6.46	10.49	8.41	8.26	-0.97	-3.13
15	1.34	6.42	10.43	8.43	8.28	-1.02	-3.15
20	1.41	6.38	10.38	8.45	8.31	-1.07	-3.18
25	1.47	6.35	10.33	8.48	8.34	-1.11	-3.22
30	1.52	6.33	10.29	8.51	8.37	-1.14	-3.27
45	1.67	6.29	10.20	8.62	8.49	-1.19	-3.45
60	1.78	6.29	10.14	8.76	8.64	-1.23	-3.65
80	1.90	6.34	10.13	8.99	8.88	-1.28	-3.92
90	1.94	6.38	10.14	9.12	9.02	-1.31	-4.05

$$*K_{\text{CaHCO}_3^+} = a_{\text{CaHCO}_3^+} / (a_{\text{Ca}^{2+}} a_{\text{HCO}_3^-})$$

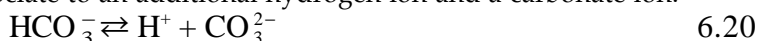
$$^\dagger K_{\text{CaCO}_3^+} = a_{\text{CaCO}_3^+} / (a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}})$$



Some of the carbonic acid dissociates to form bicarbonate and hydrogen ions:



Some of the bicarbonate will dissociate to an additional hydrogen ion and a carbonate ion:



We can write three equilibrium constant expressions for these reactions:

$$K_{\text{sp}} = \frac{a_{\text{H}_2\text{CO}_3}}{f_{\text{CO}_2}} \quad 6.21$$

$$K_1 = \frac{a_{\text{H}^+} a_{\text{HCO}_3^-}}{a_{\text{H}_2\text{CO}_3}} \quad 6.22$$

$$K_2 = \frac{a_{\text{H}^+} a_{\text{CO}_3^{2-}}}{a_{\text{HCO}_3^-}} \quad 6.23$$

The equilibrium constants for these reactions are given in Table 6.1 as a function of temperature.

In the above series of reactions, we have simplified things somewhat and have assumed that dissolved CO_2 reacts completely with water to form H_2CO_3 . This is actually not the case, and much of the dissolved CO_2 will actually be present as distinct molecular species, $\text{CO}_{2(\text{aq})}$. Thus reaction 6.18 actually consists of the two reactions:



The equilibrium for the second reaction favors $\text{CO}_{2(\text{aq})}$. However, it is analytically difficult to distinguish between the species $\text{CO}_{2(\text{aq})}$ and H_2CO_3 . For this reason, $\text{CO}_{2(\text{aq})}$ is often combined with H_2CO_3 when representing the aqueous species. The combined total concentration of $\text{CO}_{2(\text{aq})} + \text{H}_2\text{CO}_3$ is sometimes written as H_2CO_3^* . We will write it simply as H_2CO_3 .

The importance of the carbonate system is that by dissociating and providing hydrogen ions to solution, or associating and taking up free hydrogen ions, it controls the pH of many natural waters. Example 6.2 shows that pure water in equilibrium with atmospheric CO_2 will be slightly acidic. The production of free H^+ ions as a result of the solution of CO_2 and dissociation of carbonic acid plays an extremely important role in weathering. Natural waters with a pH greater than 7 must contain cations other than H^+ .

Ground waters may not be in equilibrium with the atmosphere, but will nonetheless contain some dissolved CO_2 . Because of respiration of organisms in soil (mainly plant roots & bacteria) through

CHAPTER 6: AQUATIC CHEMISTRY

EXAMPLE 6.2. pH OF WATER IN EQUILIBRIUM WITH THE ATMOSPHERE

What is the pH of water in equilibrium with the atmospheric CO_2 at 25°C , assuming ideal behavior and no other dissolved solids or gases present? The partial pressure of CO_2 in the atmosphere is 3.5×10^{-4} .

Answer: In this case, the proton balance and charge balance equations are identical:

$$[\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad 6.24$$

We cannot write a mass balance equation in this case because our system is open to the atmosphere and therefore not closed. Nevertheless, by combining equ. 6.20 with the equilibrium constant expressions, we have enough information to determine pH. By rearranging equations 6.21 through 6.23, we can make the following substitutions into 6.24:

$$[\text{HCO}_3^-] = \frac{K_1 K_{\text{sp}} P_{\text{CO}_2}}{[\text{H}^+]} \quad [\text{CO}_3^{2-}] = \frac{K_2 K_1 K_{\text{sp}} P_{\text{CO}_2}}{[\text{H}^+]^2} \quad [\text{H}_2\text{CO}_3] = K_{\text{sp}} P_{\text{CO}_2}$$

and derive the following equation:

$$[\text{H}^+]^3 - \{K_w + K_1 K_{\text{sp}} P_{\text{CO}_2}\} [\text{H}^+] - 2K_2 K_1 K_{\text{sp}} P_{\text{CO}_2} = 0 \quad 6.25$$

Substituting values from Table 6.1, we obtain:

$$[\text{H}^+]^3 - 5.308 \times 10^{-12} [\text{H}^+] - 4.9556 \times 10^{-22} = 0$$

We see that for values of pH close to neutral (i.e., $[\text{H}^+] \approx 10^{-7}$), the first term and third terms are very much smaller than the second. We can get a very good approximate answer simply by neglecting these. Doing so, we find $\text{pH} = 5.64$. The approximation is very good indeed: an exact solution using the Solver in Excel™ differs from the approximate one by less than 0.0001 pH units.

which they pass before penetrating deeper, ground waters often contain more CO_2 than water in equilibrium with the atmosphere. In addition, calcite and other carbonates are extremely common minerals in soils and in sedimentary, metamorphic, and altered igneous rocks. Ground waters will tend to approach equilibrium with calcite by either dissolving it or precipitating it:



Carbonate ions produced in this way will associate with hydrogen ions to form bicarbonate as in

EXAMPLE 6.3. pH OF A SOLUTION WITH FIXED TOTAL CARBONATE CONCENTRATION

A groundwater moving through soil into a deep aquifer acquires a total dissolved CO_2 concentration of 10^{-2} M. Assuming the water does not exchange with surrounding rock, ideal behavior and no other dissolved solids or gases, what is the pH of the water?

Answer: In this case, our charge and proton balance equations are the same as in Example 6.2, i.e., equation 6.24. Since the solution does not exchange with surrounding rock, it can be considered a closed system and we can write the following mass balance equation:

$$\Sigma \text{CO}_2 = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] = 10^{-2} \quad 6.26$$

Simultaneously solving the charge balance and mass balance equations, and using equilibrium constant expressions to eliminate carbonate and OH species, we obtain:

$$[\text{H}^+]^4 + K_1 [\text{H}^+]^3 + \{K_2 K_1 - K_w - K_1 \Sigma \text{CO}_2\} [\text{H}^+]^2 - \{K_w + 2K_2 \Sigma \text{CO}_2\} K_1 [\text{H}^+] - K_2 K_1 K_w = 0$$

We might again guess that the concentration of the carbonate ion will be very low, and that we can therefore neglect all terms in which K_2 occurs. We might also guess that pH will be acidic so that $[\text{H}^+] \gg [\text{OH}^-]$, and therefore that we can neglect terms containing K_w . Our equation becomes:

$$K_1^{-1} [\text{H}^+]^2 + [\text{H}^+] = \Sigma \text{CO}_2$$

Solving this quadratic, we find that $\text{pH} = 4.18$.

CHAPTER 6: AQUATIC CHEMISTRY

reaction 6.20 above, increasing the pH of the solution. Water containing high concentrations of calcium (and magnesium) carbonate is referred to as 'hard water'; such waters are generally somewhat alkaline.

Now suppose we have a known activity of all carbonate species in solution, say for example 10^{-2} :

$$a_{\text{H}_2\text{CO}_3} + a_{\text{HCO}_3^-} + a_{\text{CO}_3^{2-}} = \Sigma\text{CO}_2 = 10^{-2} \quad 6.28$$

From this, and the dissociation constants, we can calculate the amount of each species present as a function of pH and temperature. For example, we can use the equilibrium constant expressions to obtain substitutions for the carbonic acid and carbonate ion activities in equation 6.28 that are functions of bicarbonate ion activity and pH. We then solve equation 6.28 to obtain an expression for the activity of the bicarbonate ion as a function of total CO_2 and hydrogen ion activity:

$$a_{\text{HCO}_3^-} = \frac{\Sigma\text{CO}_2}{\frac{a_{\text{H}^+}}{K_1} + 1 + \frac{K_2}{a_{\text{H}^+}}}$$

Similar equations may be found for carbonic acid and carbonate ion. Carrying out these calculations at various pH, we can construct the graph shown in Figure 6.1. In this figure, we see that carbonic acid is the dominant species at low pH, bicarbonate at intermediate pH, and carbonate at high pH.

Particularly simple relationships occur when the activities of two species are equal. For example, choosing pH to be 6.35 (at 25°C) we can rearrange equation 6.22 and substitute to obtain:

$$\frac{a_{\text{H}^+}}{K_1} = \frac{a_{\text{H}_2\text{CO}_3}}{a_{\text{HCO}_3^-}} = \frac{10^{-6.35}}{10^{-6.35}} = 1 \quad 6.29$$

The activity of the carbonate ion will be very low at this pH. If we ignore it, equ. 6.28 becomes:

$$a_{\text{H}_2\text{CO}_3} + a_{\text{HCO}_3^-} = 10^{-2} \quad 6.30$$

According to equ. 6.30, the activities of both species are equal, so each must be 5×10^{-3} .

Now consider the point where the hydrogen ion concentration equals the bicarbonate ion concentration. At this point, the concentration of the carbonate ion is extremely low, and there is exactly enough H^+ to convert all HCO_3^- to H_2CO_3 . From the perspective of the proton balance then, the HCO_3^- concentration is equivalent to the same concentration of H_2CO_3 . This point, labelled EP on Figure 6.1, is called the CO_2 equivalence point. In a similar way, the point where the carbonic acid and bicarbonate ion concentrations are equal is called the *bicarbonate equivalence point*, and that where bicarbonate and hydroxyl concentrations are equal is called the *carbonate equivalence point*. The pH of these equivalence points depends, among other things, on the ΣCO_2 concentration.

The exact concentrations of carbonate species depends on total carbonate concentration as well as the concentration of other ions in solution. Thus the distribution shown in Figure 6.1 is unique to the conditions specified ($C_T = 10^{-2}$, no other ions present).

Nevertheless, the distribution will be qualitatively similar for other conditions.

CONSERVATIVE AND NON-CONSERVATIVE IONS

We can divide dissolved ions into *conservative* and *non-conservative* ones. The conservative ions are those whose concentrations are not affected by changes in pH, temperature, and pressure, assuming no precipitation or dissolution. In natural waters, the principal conservative ions are Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} and NO_3^- .

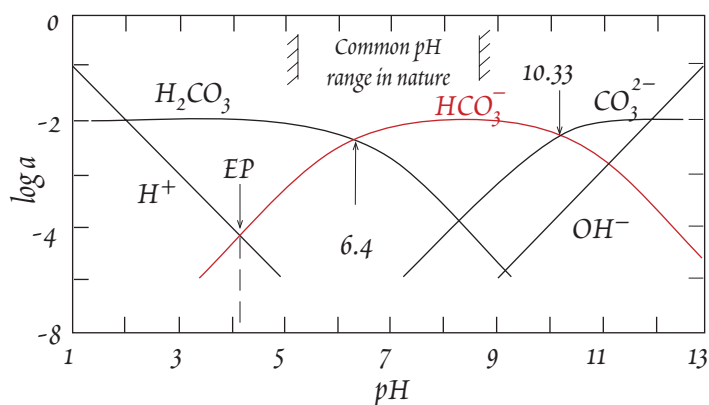


Figure 6.1. Activities of different species in the carbonate system as a function of pH assuming $\Sigma\text{CO}_2 = 10^{-2}$. After Drever (1988).

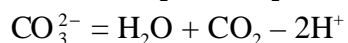
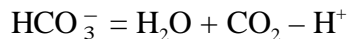
CHAPTER 6: AQUATIC CHEMISTRY

These ions are conservative because they are fully dissociated from their conjugate acids and bases over the normal range of pH of natural waters. Non-conservative ions are those that will undergo association and dissociation reactions in this pH range. These include the proton, hydroxide ion, and carbonate species as well as $\text{B}(\text{OH})_4^-$, H_3SiO_4^- , HS^- , NH_4OH , phosphate species, and many organic anions. Virtually all the non-conservative species are anions, the two principle exceptions being H^+ and NH_4OH (which dissociates to form NH_4^+ at high pH). Variations in the concentrations of non-conservative ions result from reactions between them, and these reactions can occur in the absence of precipitation or dissolution. For example, reaction of the carbonate and hydrogen ion to form bicarbonate will affect the concentrations of all three ions. Of course, if the system is at equilibrium, this reaction will not occur in the absence of an external disturbance, such as a change in temperature.

TOTAL ALKALINITY AND CARBONATE ALKALINITY

Alkalinity is a measure of acid-neutralizing capacity of a solution and is defined as the sum of the concentration (in equivalents) of bases that are titratable with strong acid. Mathematically, *we define alkalinity as the negative of TOTH when the components are the principal components of the solution at the CO_2 equivalence point*. The acidity can be defined as the negative of alkalinity, and hence equal to TOTH.

As a first example, let's consider a solution containing a fixed total dissolved concentration of CaCO_3 . At the CO_2 equivalence point, H_2CO_3 (or $\text{CO}_{2(\text{aq})}$) is the principal carbonate species, so we chose our components as H^+ , H_2O , CO_2 , and Ca^{2+} . Species HCO_3^- and CO_3^{2-} are made by combining these components as follows:



The proton mole balance equation is then:

$$\text{TOTH} = [\text{H}^+] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{OH}^-] \quad 6.31$$

The alkalinity is then:

$$\text{Alk} = -\text{TOTH} = -[\text{H}^+] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad 6.32$$

This sum, $-[\text{H}^+] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] - [\text{OH}^-]$, is called the *carbonate alkalinity*. In this example, carbonate alkalinity and alkalinity are equal since there are no other ions in solution. To avoid confusion with carbonate alkalinity, alkalinity is sometimes called *total alkalinity*.

Now let's consider a somewhat more complex example, a solution that contains H_3SiO_4^- , $\text{B}(\text{OH})_4^-$, and HS^- , and phosphoric acid (H_3PO_4 and dissociated species). This solution is similar to seawater. The corresponding components, the species actually present at the CO_2 equivalence point, are H_4SiO_4 , $\text{B}(\text{OH})_3$, H_2S , and H_2PO_4^- . Our expression for alkalinity is then (assuming negligible concentrations of S^{2-} and PO_4^{3-}):

$$\begin{aligned} \text{Alk} = & -[\text{H}^+] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \\ & + [\text{B}(\text{OH})_4^-] + [\text{H}_3\text{SiO}_4^-] + [\text{HS}^-] + [\text{H}_2\text{PO}_4^-] + 2[\text{HPO}_4^{2-}] \end{aligned} \quad 6.33$$

An analytical definition of alkalinity is that it is the quantity of acid that must be added to the solution to bring the pH to the CO_2 equivalence point.

We can also express alkalinity in terms of conservative and non-conservative ions. The charge balance equation, equation 6.11, could be written as:

$$\sum \text{cations (in equivalents)} - \sum \text{anions (in equivalents)} = 0 \quad 6.34$$

This can be expanded to:

$$\sum \text{conserv. cations} - \sum \text{conserv. anions} + \sum \text{non-conserv. cations} - \sum \text{non-conserv. anions} = 0$$

(all in units of equivalents)*. Rearranging, we have:

* One *equivalent* of a species is defined as the number of moles multiplied by the charge of the species.

CHAPTER 6: AQUATIC CHEMISTRY

$$\Sigma_{\text{conserv. cations}} - \Sigma_{\text{conserv. anions}} = -\Sigma_{\text{non-conserv. cations}} + \Sigma_{\text{non-conserv. anions}}$$

The right hand side of equation 6.32 is equal to the *alkalinity*. Hence we may write:

$$\text{Alk} = \Sigma_{\text{conserv. cations}} - \Sigma_{\text{conserv. anions}} = -\Sigma_{\text{non-conserv. cations}} + \Sigma_{\text{non-conserv. anions}} \quad 6.35$$

This equation emphasizes an important point. The difference of the sum of conservative anions and cations is clearly a conservative property, i.e., they cannot be changed except by the addition or removal of components. Since alkalinity is equal to this difference, alkalinity is also a conservative quantity (i.e., independent of pH, pressure and temperature). *Thus total alkalinity is conservative, though concentrations of individual species are not.*

Alkalinity DETERMINATION AND TITRATION CURVES

If the concentrations of all major conservative ions in a solution are known, the alkalinity can be simply calculated from equation 6.35. It is often useful, however, to determine this independently. This is done, as the definition of alkalinity suggests, through titration. Titration is the process of progressively adding a strong acid or base to a solution until a specified pH, known as an end-point, is reached. In the case of the determination of alkalinity, this end point is the CO_2 equivalence point.

Consider a solution containing a certain concentration of sodium bicarbonate (Na_2CO_3). Because the bicarbonate ion can act as a proton acceptor, NaCO_3 is a base. We can determine both the alkalinity and the total carbonate concentration of this solution by titrating with a strong acid, such as HCl. Let's examine the chemistry behind this procedure.

For clarity, we make several simplifying assumptions. First, we assume ideal behavior. Second, we assume the system is closed, so that all components are conserved, except for $[\text{H}^+]$ and $[\text{Cl}^-]$, which we progressively add. Third, we assume that the volume of our Na_2CO_3 solution is sufficiently large and our HCl sufficiently concentrated that there is no significant dilution of the original solution. Finally, we assume both Na_2CO_3 and HCl dissociate completely.

The charge balance equation during the titration is:

$$[\text{Na}^+] + [\text{H}^+] = [\text{Cl}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad 6.36$$

Since the Cl^- concentration is conservative, it will be equal to the total amount of HCl added. Into equation 6.36, we can substitute the following:

$$[\text{HCO}_3^-] = \frac{K_1[\text{H}_2\text{CO}_3]}{[\text{H}^+]} \quad 6.37a \quad [\text{CO}_3^{2-}] = \frac{K_1K_2[\text{H}_2\text{CO}_3]}{[\text{H}^+]^2} \quad 6.37b \quad \text{and} \quad [\text{OH}^-] = \frac{K_w}{[\text{H}^+]} \quad 6.37c$$

Doing so and rearranging yields:

$$[\text{Cl}^-] = [\text{Na}^+] + [\text{H}^+] - \frac{K_1[\text{H}_2\text{CO}_3]}{[\text{H}^+]} - \frac{2K_1K_2[\text{H}_2\text{CO}_3]}{[\text{H}^+]^2} - \frac{K_w}{[\text{H}^+]} \quad 6.38$$

We may also write a conservation for carbonate species, which is the same as equation 6.15 in Example 6.1. Substituting equations 6.37a and 6.37b into 6.15 and rearranging, we have:

$$[\text{H}_2\text{CO}_3] = \frac{\Sigma\text{CO}_2}{1 + \frac{K_1}{[\text{H}^+]} + \frac{K_1K_2}{[\text{H}^+]^2}} \quad 6.39$$

Substituting this expression into 6.38, we obtain:

$$[\text{Cl}^-] = [\text{Na}^+] + [\text{H}^+] - \frac{\Sigma\text{CO}_2}{[\text{H}^+] + K_1 + \frac{K_1K_2}{[\text{H}^+]}} \left\{ K_1 + \frac{2K_1K_2}{[\text{H}^+]} \right\} - \frac{K_w}{[\text{H}^+]} \quad 6.40$$

Thus one equivalent of CO_3^{2-} is equal to 0.5 moles of CO_3^{2-} , but one equivalent of Cl^- is equal to 1 mole of Cl^- . For an acid or base, an equivalent is the number moles of the substance divided by the number of hydrogen or hydroxide ions that can be potentially produced by dissociation of the substance. Thus there are 2 equivalents per mole of H_2CO_3 , but 1 equivalent per mole of NaOH .

EXAMPLE 6.4. Calculating Alkalinity of Spring Water

Calculate the alkalinity of spring water from Thonon, France, whose analysis is given at right (this is the same analysis as in Problem 3.8).

Answer: We can use equation 6.34 to calculate alkalinity. All the ions listed here are conservative with the exception of HCO_3^- . To calculate alkalinity, we first need to convert the molar concentrations to equivalents; we do so by multiplying the concentration of each species by its charge. We find the sum of conservative anion concentrations to be 0.749 meq (milliequivalents), and that of the conservative cation concentrations to be 6.733 meq. The alkalinity is the difference, 5.985 meq.

Anions	mM	Cations	mM
HCO_3^-	5.436	Ca^{2+}	2.475
SO_4^{2-}	0.146	Mg^{2+}	0.663
NO_3^-	0.226	K^+	0.036
Cl^-	0.231	Na^+	0.223

From stoichiometry, we also know that $\Sigma\text{CO}_2 = 0.5[\text{Na}^+]$. From this equation we can construct a plot showing how many moles of HCl we must add to achieve a certain pH. We can also use equation 6.39 and similar ones expressing the bicarbonate and carbonate ions as functions of pH to plot the change in the carbonate speciation during the titration. Figure 6.2 shows such a plot for a 0.005 M Na_2CO_3 solution. There are two regions where pH changes rapidly with small additions of HCl. These are the two end-points of the titration. Comparing the titration curve with the speciation curves, we see that the two end-points correspond to the CO_2 and bicarbonate equivalence points.

An analytical definition of alkalinity is its *acid neutralizing capacity when the end-point of the titration is the CO_2 equivalence point* (Morel and Hering, 1993). We had previously defined alkalinity as the negative of *TOTH* when the principal components are those at the CO_2 equivalence point. Let's now show that these definitions are equivalent.

In Example 6.1, we found that the *TOTH* expression for a Na_2CO_3 solution is:

$$\text{TOTH} = [\text{H}^+] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{OH}^-] \quad (6.13)$$

and the charge balance equation (before any HCl is added) is:

$$[\text{Na}^+] + [\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad (6.14)$$

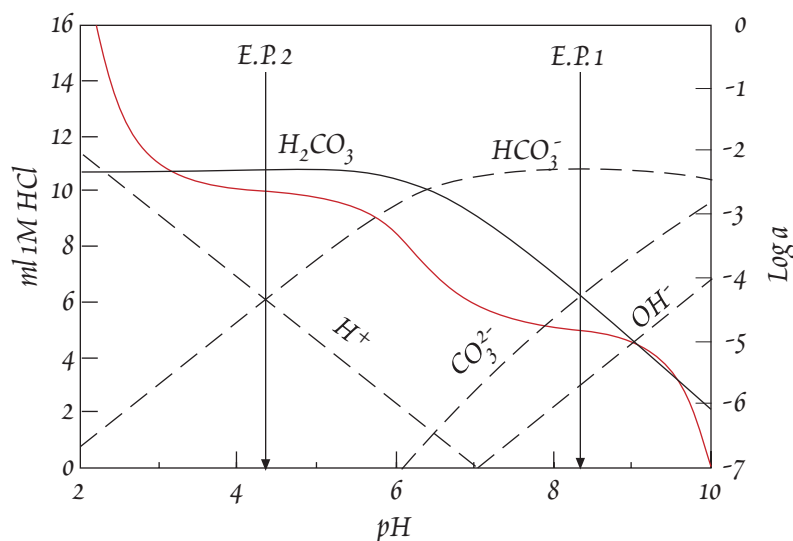


Figure 6.2. Titration curve (solid red line) for a one liter 0.005 M Na_2CO_3 solution titrated with 1M HCl. Left axis shows the number of ml of HCl to be added to obtain a given pH. Also shown are the concentrations of carbonate species, H^+ , and OH^- (dashed black lines, right axis gives scale).

Combining the two we have:

$$\text{TOTH} = -[\text{Na}^+]$$

Since the alkalinity is the negative of *TOTH*, it follows that:

$$\text{Alk} = [\text{Na}^+] \quad 6.41$$

We obtain exactly the same result from equation 6.35. It is easy to show that after titrating to the CO_2 equivalence point, the alkalinity is 0. The change in alkalinity is thus equal to the number of equivalents, or moles, of H^+ we have added to the solution. Since at the end point, $[\text{H}^+] = [\text{HCO}_3^-]$ and the concentrations of CO_3^{2-} and OH^- are negligible, our charge balance equation, 6.36, reduces to:

$$[\text{Na}^+] = [\text{Cl}^-]$$

Comparing this with 6.41, we

CHAPTER 6: AQUATIC CHEMISTRY

see that the alkalinity is equal to the amount of HCl added. In the example in Figure 6.2, the equivalence point occurs after the addition of 10 ml of 1M HCl, or a total of 0.01 moles of Cl^- . (Notice that since at the end points, small additions of acid result in large changes in pH, we do not have to determine pH particularly accurately during the titration for an accurate determination of alkalinity.) So the alkalinity is 0.01 equivalents. This is exactly the answer we obtain from 6.41 for 1 liter of 0.005 M Na_2CO_3 since there are 2 moles of Na^+ for each mole of Na_2CO_3 .

By assuming that the concentration of H^+ contributes negligibly to charge balance, it is also easily shown (Problem 6.2) that at the bicarbonate equivalence point:

$$\Sigma\text{CO}_2 = [\text{Cl}^-] + [\text{OH}^+] \quad 6.42$$

Thus total carbonate is obtained by titrating to the bicarbonate equivalence point (knowing the pH of the end-point allows us to determine the ΣCO_2 exactly; however neglecting the $[\text{OH}^-]$ term in 6.42 results in only a 1% error in the example shown). In Figure 6.2, this occurs after the addition of 5 ml 1M HCl.

BUFFER INTENSITY

The carbonate system is a good example of a pH *buffer*. We define the *buffer intensity* of a solution as the inverse of change in pH per amount of strong base (or acid) added:

$$\beta \equiv \frac{dC_B}{d\text{pH}} = -\frac{dC_A}{d\text{pH}} \quad 6.43$$

where C_B and C_A are the concentrations, in equivalents, of strong base or acid respectively. Thus the greater the buffer capacity of a solution, the less change in its pH as an acid or base is added. The buffer capacity of a solution can be calculated by differentiation of the equation relating base (or acid) concentration to pH, as is illustrated in Example 6.5.

In nature, a pH buffer acts to control pH within a narrow range even though H^+ ions might be added or taken out of solution by other reactions. To understand how this works, imagine a solution containing carbonic acid, carbonate, bicarbonate, and hydrogen ions in equilibrium concentrations. Now imagine that additional H^+ ions are added (for example, by addition of rain water containing HNO_3). In order for the right hand side of equation 6.22 to remain equal to K_1 despite an increase in the activity of H^+ (which it must at constant temperature and pressure), the bicarbonate activity must decrease and the carbonic acid activity increase. It is apparent then that reaction 6.19 must be driven to the left, taking free hydrogen ions from solution, hence driving the pH back toward its original value. Similarly, reaction 6.20, the dissociation of bicarbonate, will also be driven to the left, increasing the bicarbonate concentration and decreasing the hydrogen and carbonate ion concentrations.

The buffer capacity of the carbonate system depends strongly on pH and also on the concentration of the carbonate species and the concentration of other ions in solution. In pure water containing no other ions and only carbonate in amounts in equilibrium with the atmosphere, the buffering capacity is negligible near neutral pH, as is shown in Figure 6.4. Natural solutions, however, can have substantial buffering capacity. Figure 6.3 illustrates three other examples of

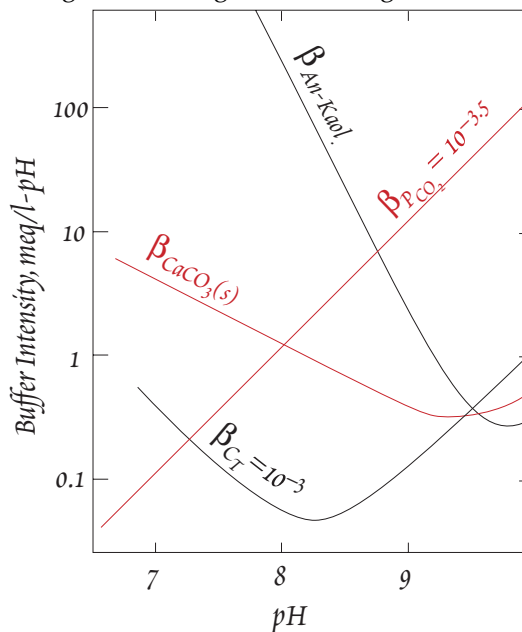


Figure 6.3. Buffer intensity as a function of pH for several ideal natural systems: β_{CT} fixed total dissolved CO_2 , β_{PCO_2} water in equilibrium with atmospheric CO_2 , $\beta_{\text{CaCO}_3(s)}$ water in equilibrium with calcite, and $\beta_{\text{An-Kaol.}}$ water in equilibrium with anorthite and kaolinite. After Stumm and Morgan (1996).

EXAMPLE 6.5. CALCULATING BUFFER INTENSITY

How pH will change for given addition of a strong base such as NaOH for a solution of pure water in equilibrium with atmospheric CO₂? Calculate the buffer intensity of this solution as a function of pH. Assume that NaOH completely dissociates and ideal behavior.

Answer: We want to begin with the charge balance equation in this case because it relates the two quantities of interest in this case, [Na⁺] and [H⁺]. The charge balance equation is the same as in Example 6.1:

$$[\text{Na}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] \quad (6.14)$$

Since Na⁺ is a conservative ion, its concentration will depend only on the amount of NaOH added, so that C_B = [Na⁺]. Substituting this into equation 6.37 and rearranging, we have:

$$C_B = [\text{OH}^-] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] - [\text{H}^+] \quad 6.44$$

We can now use the equilibrium constant relations to substitute for the first three terms of the right hand side of 6.44 and obtain:

$$C_B = + \frac{K_W + K_1 K_{sp} P_{\text{CO}_2}}{[\text{H}^+]} + 2 \frac{K_2 K_1 K_{sp} P_{\text{CO}_2}}{[\text{H}^+]^2} - [\text{H}^+]$$

Using the relation pH = -log [H⁺] to replace [H⁺] in this equation with pH, we have:

$$C_B = + \frac{K_W + K_1 K_{sp} P_{\text{CO}_2}}{10^{-\text{pH}}} + 2 \frac{K_2 K_1 K_{sp} P_{\text{CO}_2}}{10^{-2\text{pH}}} - 10^{-\text{pH}}$$

Now differentiating with respect to pH, we obtain:

$$\frac{dC_B}{dpH} = \beta = \ln 10 ([K_W + K_1 K_{sp} P_{\text{CO}_2}] 10^{\text{pH}} + 4 K_2 K_1 K_{sp} P_{\text{CO}_2} 10^{2\text{pH}} + 10^{-\text{pH}}) \quad 6.45$$

Figure 6.4 shows a plot of this equation using the values in Table 6.1. Buffer intensity is negligible in neutral to slightly acidic conditions, but increases rapidly with pH.

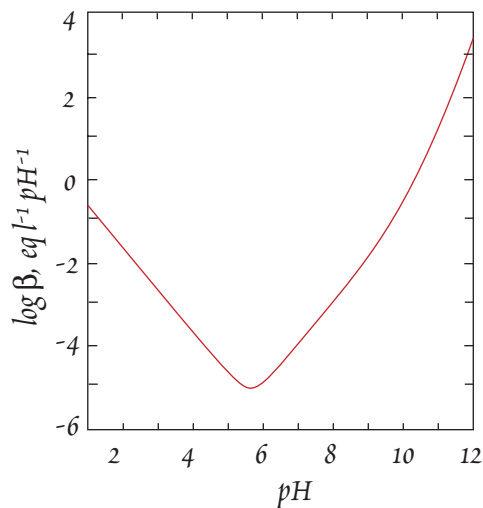


Figure 6.4. Buffer capacity of a carbonate solution in equilibrium with atmospheric CO₂.

natural pH buffers. "Hard water" is an example of a water with a substantial buffering capacity due to the presence of dissolved carbonates. As we shall see, how adversely lakes and streams are impacted by "acid rain" depends on their buffering intensity.

COMPLEXATION

Ions in solution often associate with other ions, forming new species called complexes. Complex formation is important because it affects the solubility, as will see in the following section, and reactivity of ions. In some cases, complex formation is an intermediate step in the precipitation process. In other cases, ions form stable, soluble complexes that greatly enhance the solubility of the one or both of the ions.

Complexation is usually described in terms of a central ion, generally a metal, and ions or molecules that surround, or *coordinate*, it, referred to as *ligands*. Perhaps the simplest and most common complexes are those formed between metals and water or its dissociation products. We learned in Chapter 3 that ions in aqueous solutions are surrounded by a solvation shell. The solvation shell (Figure 3.11) consists of water molecules, typically 6, though fewer in some cases, loosely bound to the ion

CHAPTER 6: AQUATIC CHEMISTRY

through electrostatic forces. This solvation shell is referred to as an *aquo complex*. Water molecules are the ligands in aquo-complexes. Aquo-complexes are ubiquitous: all charged species will have a solvation shell. Truly “free ions” do not exist: ions not otherwise complexed and referred to as “free ions” are in reality associated with surrounding water molecules and hence actually aquo-complexes. However, the existence of this type of complex is implicitly accounted for through the activity coefficient and not usually explicitly considered. Nevertheless, it is important to bear in mind that since all ions are complexed in some way to begin with, every complexation reaction in aqueous solution is essentially a ligand exchange reaction.

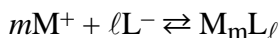
Beyond aquo complexes, we can distinguish two types of complexes:

- *Ion pairs*, where ions of opposite charge associate with one and other through electrostatic attraction, yet each ion retains part or all of its solvation sphere. Figure 6.5 illustrates two possibilities: one where the two solvation spheres are merely in contact, the other where the water molecules are shared between the two solvation spheres. Ion pairs are also called *outer sphere complexes*.

- *Complexes (senso stricto)*, where the two ions are in contact and a bond forms between them that it at least partly covalent in nature (Figure 6.5c). These are often called *inner sphere complexes*.

STABILITY CONSTANTS

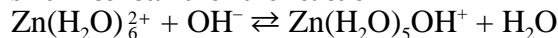
In its simplest form, the reaction for the formation of an ion pair or complex between a metal cation M and an anion or ligand L may be written as:



As with any other reaction, we may define an equilibrium constant as:

$$K = \frac{a_{M_m L_{\ell}}}{a_M^m a_L^{\ell}} \quad 6.46$$

For example, the equilibrium constant for the reaction:



is:

$$K_1 = \frac{a_{ZnH_2O_5OH^{+}}}{a_{Zn(H_2O)_6^{2+}} a_{OH^{-}}}$$

(we omit the activity of water because we assume, as usual, that it is 1). As we noted, however, the aquo-complex is generally not explicitly expressed, so this same reaction would more often be written as:

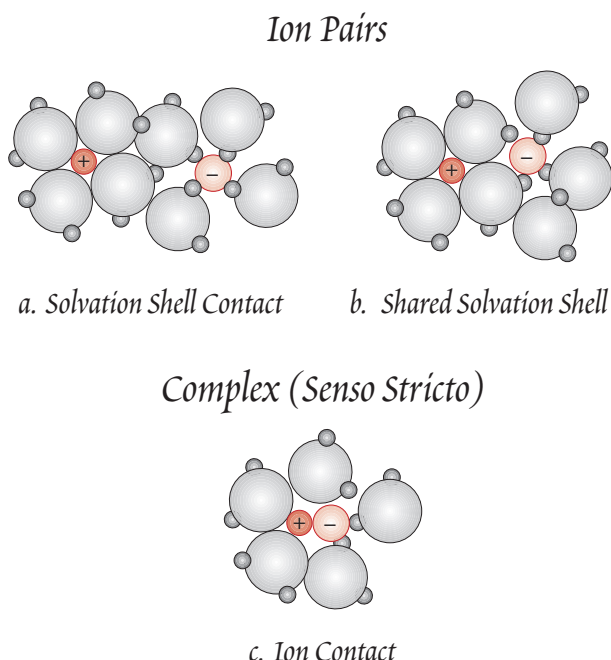
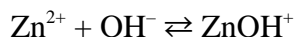


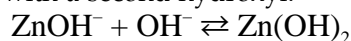
Figure 6.5. Illustration of ion pair and complex formation. Two types of ion pairs can be envisioned: (a) solvation shell contact and (b) solvation shell sharing. Ion pairs are sometimes referred to as outer sphere complexes. In formation of true complexes, ions are in contact (c) and there is some degree of covalent bonding between them. These are sometimes referred to as inner sphere complexes.

CHAPTER 6: AQUATIC CHEMISTRY

and the equilibrium constant as:
$$K_1 = \frac{a_{\text{ZnOH}^+}}{a_{\text{Zn}^{2+}}a_{\text{OH}^-}}$$

Equilibrium constants for complex formation reactions are often referred to as *stability constants*, since their value is an indication of the stability of the complex, and often denoted by β . Thus for the reaction above, β_1 and K_1 are synonymous. *By convention, stability constants are written so as the complex appears in the numerator (i.e., as a product of the reaction).*

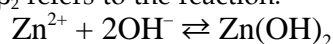
The zinc ion might associate with a second hydroxyl:



The equilibrium constant is:

$$K_2 = \frac{a_{\text{Zn(OH)}_2}}{a_{\text{ZnOH}^+}a_{\text{OH}^-}}$$

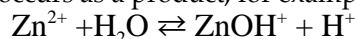
Here, however, the notation for the stability constant and the equilibrium constant differs. Whereas K_2 refers to the reaction above, β_2 refers to the reaction:



Hence:

$$\beta_2 = \frac{a_{\text{Zn(OH)}_2}}{a_{\text{Zn}^{2+}}a_{\text{OH}^-}^2} = K_1 K_2$$

Finally, the notation $*K$ and $*\beta$ are sometimes used for reactions in which the complexation reactions written so as the hydrogen ion occurs as a product, for example:



and:

$$*K_1 = \frac{a_{\text{ZnOH}^+}a_{\text{H}^+}}{a_{\text{Zn}^{2+}}}$$

$*K_1$ is then related to K_1 as: $*K_1 = K_1 K_w = *\beta_1$

where K_w is the dissociation constant for water (10^{-14}).

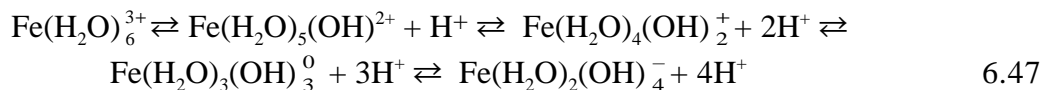
We can, of course, define *apparent* equilibrium and stability constants, where the molar concentrations are used in place of activity. Indeed, as in other aspects of geochemistry, apparent equilibrium constants are more commonly encountered than true ones.

The equilibrium constant may in turn be related to the Gibbs Free Energy of the reaction, as in equation 3.98. Interestingly, the free energy changes involved in complexation reactions result largely from entropy changes. Indeed, the enthalpy changes of many complexation reactions are unfavorable, and the reaction proceeds only because of large positive entropy changes. These entropy changes result from the displacement of water molecules from the solvation shell.

The link between the equilibrium constant and the free energy change is particularly important and useful in complexation reactions because it is in most instances difficult to determine the concentrations of individual complexes analytically. Thus on knowledge of chemical speciation in natural waters derived largely from predictions based on equilibrium thermodynamics.

WATER-RELATED COMPLEXES

Let's consider further the types of complexes typically found in aqueous solution. Ferric iron, for example, will form a $\text{Fe(H}_2\text{O)}_6^{3+}$ complex at relatively low pH. The positive charge of the central ion tends to repel hydrogens in the water molecules, so that water molecules in these aquo-complexes are more readily hydrolyzed than otherwise. Thus these aquo-complexes can act as weak acids. For example:



As reaction 6.47 suggests, equilibrium between these *hydroxo-complexes* depends strongly on pH.

CHAPTER 6: AQUATIC CHEMISTRY

The repulsion between the central metal ion and protons in water molecules of the solvation shell will increase with decreasing diameter of the central ion (decreasing distance between the protons and the metal) and with increasing charge of the central ion. For highly charged species, the repulsion of the central ion sufficiently strong that all hydrogens are repelled and it is surrounded only by oxygens. Such complexes, for example, MnO_4^- and CrO_4^{2-} , are known as *oxo-complexes*. Intermediate types in which the central ion is surrounded, or *co-ordinated*, by both oxygens and hydroxyls are also possible, for example $\text{MnO}_3(\text{OH})$ and $\text{CrO}_3(\text{OH})^-$, and are known as hydroxo-oxo complexes. Figure 6.6 summarizes the predominance of aquo, hydroxo, hydro-oxo, and oxo complexes as a function of pH and valance state. For most natural waters, metals in valance states I and II will be present as “free ions”, i.e., aquo complexes, valance III metals will be present as aquo and hydroxo complexes, those with higher charge will present as oxo-complexes.

Polynuclear hydroxo- and oxo-complexes, containing two or more metal ions, are also possible, for example:

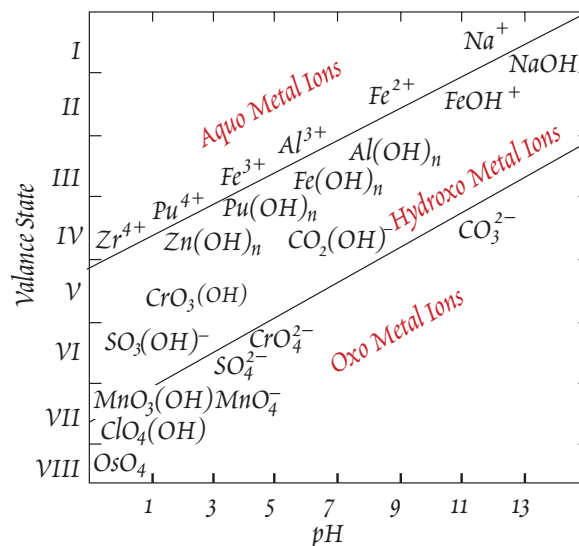
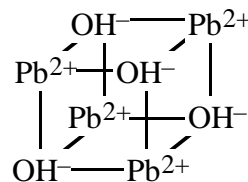
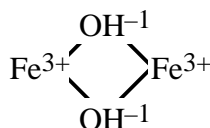
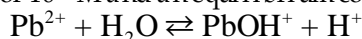


Figure 6.6. Predominant aquo, hydroxo, and oxo complexes as a function of pH and valance state. After Stumm and Morgan (1996).

EXAMPLE 6.6. COMPLEXATION OF Pb

Assuming a Pb concentration of 10^{-8} M and an equilibrium constant for the reaction:



of $10^{-7.7}$, calculate the fraction of Pb that will be present as PbOH^+ from pH 5 to 8.

Answer: In addition to the above reaction, we also need the conservation equation for Pb:

$$\Sigma \text{Pb} = \text{Pb}^{2+} + \text{PbOH}^+$$

The equilibrium constant expression is:

$$K = \frac{[\text{PbOH}^+][\text{H}^+]}{\text{Pb}^{2+}}$$

Solving the conservation equation for Pb^{2+} and substituting into the equilibrium constant expression, we obtain:

$$(\Sigma \text{Pb} - [\text{PbOH}^+])K = [\text{PbOH}^+][\text{H}^+]$$

With some rearranging, we eventually obtain the following expression:

$$[\text{PbOH}^+]/\Sigma \text{Pb} = \frac{K}{[\text{H}^+] + K}$$

The result is illustrated in Figure 6.7. Below pH 6, virtually all Pb is present as Pb^{2+} , above pH 9, virtually all Pb is present as PbOH^+ .

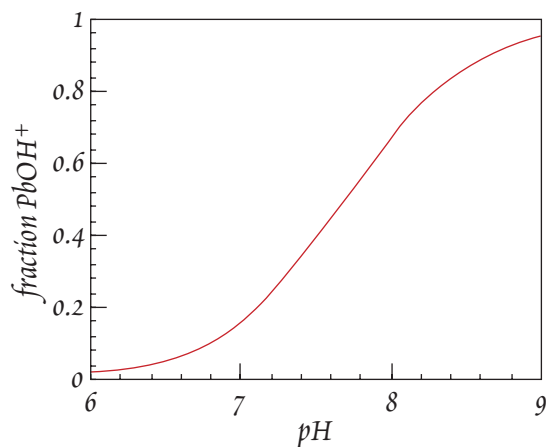
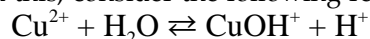


Figure 6.7. Fraction of Pb complexed as PbOH^+ as a function of pH.

CHAPTER 6: AQUATIC CHEMISTRY

As one might expect, the extent to which such *polymeric* species form depends on the concentration of the metal ion concentration: they become increasingly common as concentration increases. Most highly charged (3+ and higher oxidation states) metal ions are highly insoluble in aqueous solution. This is due in part to the readiness with which they form hydroxo-complexes, which can in turn be related to the dissociation of surrounding water molecules as a result of their high charge. When such ions are present at high concentration, formation of polymeric species such as those above quickly follows formation of the hydroxo complex. At sufficient concentration, formation of these polymeric species leads to the formation of colloids and ultimately to precipitation. In this sense, these polymeric species can be viewed as intermediate products of precipitation reactions.

Interestingly enough, however, the tendency of metal ions to hydrolyze decreases with concentration. The reason for this is the effect of the dissociation reaction on pH. For example, increasing the concentration of dissolved copper decreases the pH, which in turn tends to drive the hydrolysis reaction to the left. To understand this, consider the following reaction:



for which the apparent equilibrium constant is $K^{\text{app}} = 10^{-8}$. We can express the fraction of copper present as CuOH^+ , α_{CuOH^+} as:

$$\alpha = \frac{[\text{CuOH}^+]}{\text{Cu}_T} = \frac{K}{[\text{H}^+] + K} \quad 6.48$$

where Cu_T is the total dissolved copper. At constant pH, the fraction of Cu complexed is constant. However, for a solution with a fixed amount of Cu ion dissolved, we can also write a proton balance equation:

$$[\text{H}^+] = [\text{CuOH}^+] + [\text{OH}^-]$$

a charge balance equation, and a mass balance equation. Combining these with the equilibrium constant expression, we can calculate both α and pH as a function of Cu_T (Problem 6.9). When we do this, we see that upon dilution, as Cu_T increases, both pH and α decrease, as is demonstrated in Figure 6.8.

OTHER COMPLEXES

When non-metals are present in solution, as they would inevitably be in natural waters, then other complexes are possible. In this respect we can divide the elements into four classes (Table 6.2, Figure 6.9). The first is the non-metals, which form anions or anion groups. The second group is the "A-type" or "hard" metals. These metals, listed in Table 6.2, have spherically symmetric, inert-gas type outer electron configurations. Their electron shells are not readily deformed by electric fields and can be viewed as "hard spheres". Metals in this group preferentially forms complexes with fluorine and ligands having oxygen as the donor atoms (e.g., OH^- ,

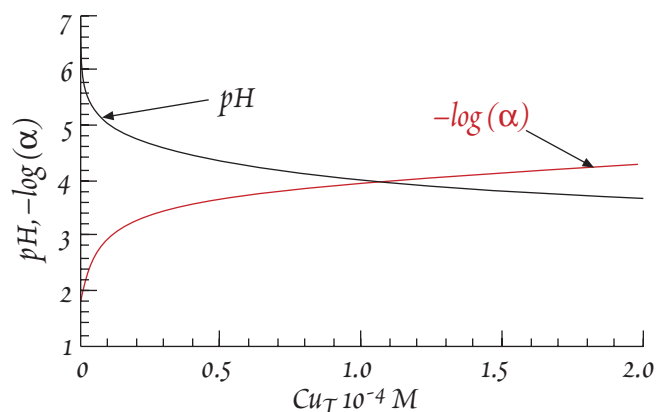


Figure 6.8. pH and $-\log \alpha$, as a function of total copper concentration in aqueous solution. α is the fraction of copper present as the hydroxo-complex.

Table 6.2. Classification of METAL IONS

A-Type Metals

Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} ,
 Ba^{2+} , Al^{3+} , Sc^{3+} , Y^{3+} , REE, Ti^{4+} , Si^{4+} , Zr^{4+} ,
 Hf^{4+} , Th^{4+} , Nb^{5+} , Ta^{5+} , U^{6+}

B-Type Metals

Cu^{2+} , Ag^+ , Au^+ , Tl^+ , Ga^+ , Zn^{2+} , Cd^{2+} ,
 Hg^{2+} , Pb^{2+} , Sn^{2+} , Ti^{3+} , Au^{3+} , In^{3+} , Bi^{3+}

Transition Metal Ions

V^{2+} , Cr^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} ,
 Cu^{2+} , Ti^{3+} , V^{3+} , Cr^{3+} , Mn^{3+} , Fe^{3+} , Co^{3+}

From Strumm and Morgan (1996).

CHAPTER 6: AQUATIC CHEMISTRY

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rd
Fr	Ra	Ac	\														
\			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
\			Ac	Th	Pa	U	Np	Pu									

A-Metals

Transition Metals

B Metals

Ligand Formers

Figure 6.9. Classification of the elements with respect to complex formation in aqueous solution.

CO_3^{2-} , PO_4^{3-} , SO_4^{2-}). Stability of the complexes formed by these metals increases with charge to radius ratio. Thus the alkalis form only weak, unstable complexes, while elements such as Zr^{4+} form very strong, stable complexes (e.g., with fluoride). In complexes formed by A-type metals, anions and cations are bound primarily by electrostatic forces, i.e., ionic-type bonds. The A-type elements correspond approximately to the lithophile elements of Goldschmidt's classification presented in Chapter 7.

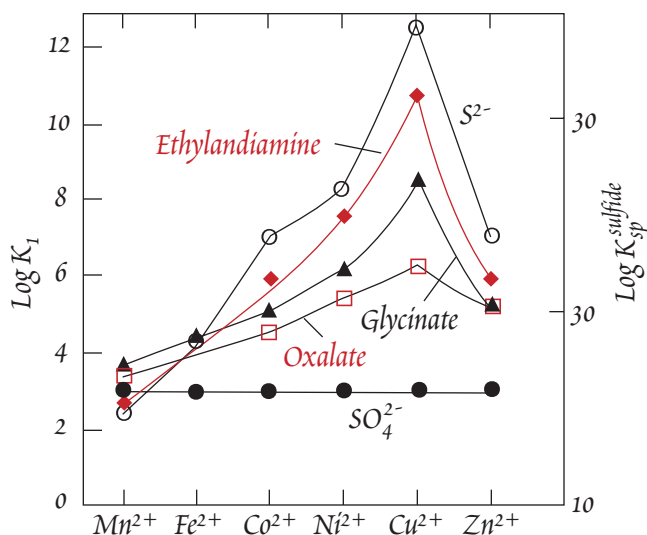


Figure 6.10. Stability constants for transition metal sulfate and organic complexes and their sulfide solubility constants, illustrating the Irving-Williams series. From Strumm and Morgan (1996).

The third group is the B-type, or "soft", metal ions. Their electron sheaths are not spherically symmetric and are readily deformed by the electrical fields of other ions (hence the term soft). They preferentially form complexes with bases having S, I, Br, Cl, or N (such as ammonia; not nitrate) as the donor atom. Bonding between the metal and ligand(s) is primarily covalent and is comparatively strong. Thus Pb form strong complexes with Cl^- and S^{2-} . Many of the complexes formed by these elements are quite insoluble. The B-type elements consist primarily of the "chalcophile elements", a term we will define in the next chapter.

The first series transition metals form the fourth group, and correspond largely to the siderophile elements. Their electron sheaths are not spherically symmetric, but they are not so readily polarizable as the B-type metals. On the whole however,

CHAPTER 6: AQUATIC CHEMISTRY

their complex-forming behavior is similar to that of the B-type metals.

Among the transition metals, the sequence of complex stability is $\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$, a sequence known as the Irving-Williams Series. This is illustrated in Figure 6.10. In that figure, all the sulfate complexes have approximately the same stability, a reflection of the predominately electrostatic bonding between sulfate and metal. Pronounced differences are observed for organic ligands. The figure demonstrates an interesting feature of organic ligands: although the absolute value of stability complexes varies from ligand to ligand, the relative affinity of ligands having the same donor atom for these metals is always similar.

Organic molecules can often have more than one functional group and hence can coordinate a metal at several positions, a process called chelation. Such ligands are called *multi-dentate* and organic compounds having this properties are referred to as chelators or chelating agents. We will explore this topic in greater detail in the Chapter 14.

The kinetics of complex formation is quite fast in most cases, so that equilibrium can be assumed. There are exceptions, however. As we noted earlier in this section, all complexation reactions are ligand exchange reactions: water playing the role of ligand in “free ions”. The rate at which complexes form is thus governed to a fair degree by the rate at which water molecules are replaced in the hydration sphere.

COMPLEXATION IN FRESH WATERS

Where only one metal is involved, the complexation calculations are straightforward, as exemplified in Example 6.6. Natural waters, however, contain many ions. The most abundant of these are Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , HCO_3^- , CO_3^{2-} , and there are many possible complexes between them as well as with H^+ and OH^- . To calculate the speciation state of such solutions an iterative approach is required. The calculation would be done as follows. First, we need the concentrations, activity coefficients, and stability constants (or apparent stability constants) for all species. Then we assume all ions are present as free ions and calculate the concentrations of the various possible complexes on this basis. In this pass, we need only consider the major ions (we can easily understand why with an example: formation of PbCl^+ when the concentration of Pb is 10^{-8} or less and the abundance of Cl^- is 10^{-4} or more will have an insignificant affect on the free ion Cl concentration). We then iterate the calculation, starting with the free ion concentrations corrected for abundances of complexes we calculated in the previous iteration. This process is repeated until two successive iterations produce the same result. Although it sounds difficult, such calculations typically converge within 2 to 4 iterations. Example 6.7 shows how this is done. Once free ion concentrations of the major ligands are known, the speciation of trace metals may be calculated.

As Example 6.7 demonstrates, the major metals in fresh waters are present mainly as free ions (aquocomplexes), as are the three most common anions, chloride, sulfate, and bicarbonate. The alkali and alkaline earth trace elements are also largely uncomplexed. Co^{2+} , Ni^{2+} , Zn^{2+} , Ag^+ , and Cd^{2+} are roughly 50% complexed. The remaining metals are present as primarily as complexes. B, V, Cr, Mo, and Re, as well as As and Se are present as anionic oxo-complexes. Other metals are usually present as hydroxide, carbonate, chloride, or organic complexes. Under reducing conditions, HS^- and S^{2-} complexes are important. In organic-rich waters such as swamps, organic complexes can be predominant. We will discuss organic complexes in more detail in Chapter 14, and speciation in seawater in Chapter 15.

DISSOLUTION AND PRECIPITATION REACTIONS

DISSOLUTION OF CARBONATES BY GROUND AND SURFACE WATERS

Calcium carbonate is an extremely common component of sedimentary rocks and is found present in weathered igneous and metamorphic rocks. It is also a common constituent of many soils. Water passing through such soils and rocks will precipitate or dissolve calcite until equilibrium is achieved. This process has a strong influence on carbonate concentrations, hardness, and pH as well as dissolved calcium ion concentrations. Let's examine calcite solubility in more detail.

CHAPTER 6: AQUATIC CHEMISTRY

EXAMPLE 6.7. SPECIATION IN FRESH WATER

Using the water and stability constants given in the adjacent tables, calculate the activities of the major species in this water.

Answer: The first two problem we need to address are the nature of the carbonate species and activity

coefficients. At this pH, we can see from Figure 6.1 that bicarbonate will be the dominant carbonate species. Making the initial assumption that all carbonate is bicarbonate, we can calculate ionic strength and activity coefficients using the Debye-Hückel Law (equation 3.84). These are shown in the table below. Having the activity coefficients, we can calculate the approximate abundance of the carbonate ion assuming all carbonate is bicarbonate:

$$[\text{CO}_3^{2-}] = \frac{\gamma_{\text{HCO}_3^-} \Sigma \text{CO}_2}{K_{\text{aH}} \gamma_{\text{CO}_3^{2-}} + \gamma_{\text{HCO}_3^-}} \quad 6.49$$

(this equation is readily derived from conservation and the equilibrium constant expression). The bicarbonate ion is then calculated as:

$$[\text{HCO}_3^-] = \Sigma \text{CO}_2 - [\text{CO}_3^{2-}]$$

The result confirms our initial first order assumption that all carbonate is present as bicarbonate.

Using the concentrations and stability constants given as well as the activity coefficients we calculated, we can then make a first pass at calculating the concentrations of the complexes. For example, MgCO_3 is calculated as

$$a_{\text{MgCO}_3} = \beta_{\text{MgCO}_3} a_{\text{Mg}^{2+}} a_{\text{CO}_3^{2-}}$$

The results of this first iteration are shown in a matrix. Chlorine does not complex with any of the major ions to any significant degree, so we can neglect it in our calculations.

We then correct the free ion activities by subtracting the activities of the complexes they form. Thus for example, the corrected free ion activity of Mg^{2+} is calculated as:

$$a_{\text{Mg}^{2+}}^{\text{corr}} = a_{\text{Mg}^{2+}}^{\text{ini}} - a_{\text{MgOH}^+} - a_{\text{MgHCO}_3^+} - a_{\text{MgCO}_3} - a_{\text{MgSO}_4}$$

We then repeat the calculation of the activities of the complexes using these corrected free ion activities. A second matrix shows the results of this second iteration. A third table shows the percent of each ion present as a free ion (aquo complex). In fresh waters such as this one, most of the metals are present as free ions, the alkaline earths being 5% complexed by sulfate and carbonate.

Analysis of STREAM WATER (mM)

Na^+	0.32	Cl^-	0.22
K^+	0.06	SO_4^{2-}	0.12
Mg^{2+}	0.18	ΣCO_2	1.0
Ca^{2+}	0.36	pH	8.0

Log Stability Constants

	OH^-	HCO_3^-	CO_3^{2-}	SO_4^{2-}	Cl^-
H^+	14	6.35	10.33	1.99	—
Na^+	—	-0.25	1.27	1.06	—
K^+	—	—	—	0.96	—
Mg^{2+}	2.56	1.16	3.4	2.36	—
Ca^{2+}	1.15	1.26	3.2	2.31	—

ION ACTIVITIES: ITERATION 1

	free ion	OH^-	HCO_3^-	CO_3^{2-}	SO_4^{2-}
free ion		1×10^{-06}	9.17×10^{-04}	6.79×10^{-07}	1.62×10^{-04}
H^+	1×10^{-08}	—	2.12×10^{-05}	9.46×10^{-04}	1.75×10^{-10}
Na^+	3.03×10^{-04}	—	1.62×10^{-07}	2.51×10^{-08}	6.27×10^{-07}
K^+	5.69×10^{-05}	—	—	—	9.33×10^{-08}
Mg^{2+}	1.39×10^{-04}	5.09×10^{-08}	2.03×10^{-06}	1.65×10^{-06}	6.10×10^{-06}
Ca^{2+}	2.77×10^{-04}	4.29×10^{-09}	5.08×10^{-06}	2.07×10^{-06}	1.08×10^{-05}

ION ACTIVITIES: ITERATION 2

	free ion	OH^-	HCO_3^-	CO_3^{2-}	SO_4^{2-}
free ion		1×10^{-06}	9.12×10^{-04}	1.12×10^{-06}	1.65×10^{-04}
H^+	1×10^{-08}	—	2.06×10^{-05}	9.12×10^{-04}	1.58×10^{-10}
Na^+	3.03×10^{-04}	—	1.57×10^{-07}	2.35×10^{-08}	5.64×10^{-07}
K^+	5.69×10^{-05}	—	—	—	8.40×10^{-08}
Mg^{2+}	1.40×10^{-04}	5.03×10^{-08}	1.84×10^{-06}	1.45×10^{-06}	5.14×10^{-06}
Ca^{2+}	2.80×10^{-04}	3.92×10^{-09}	4.64×10^{-06}	1.83×10^{-06}	9.16×10^{-06}

% FREE ION

Na^+	99.76%	Cl^-	100%
K^+	99.85%	SO_4^{2-}	91.7%
Mg^{2+}	94.29%	HCO_3^-	99.3%
Ca^{2+}	94.71%	CO_3^{2-}	25.3%

CHAPTER 6: AQUATIC CHEMISTRY

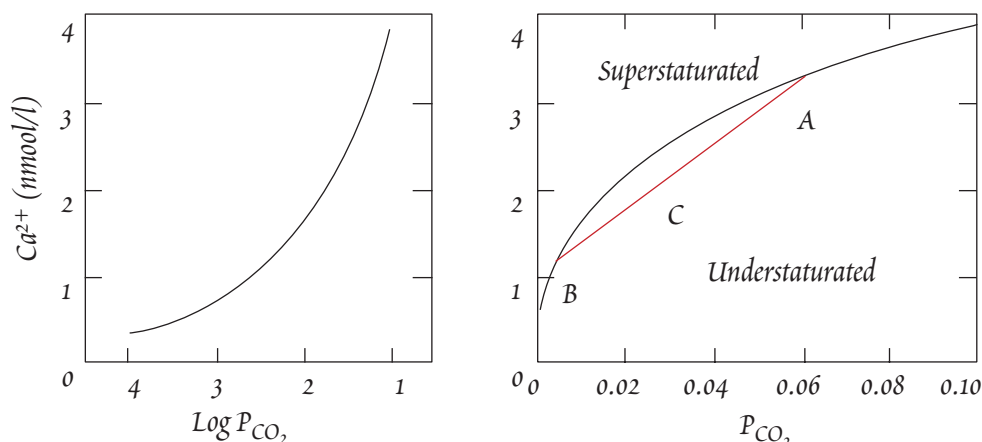


Figure 6.11. Concentration of calcium ion in equilibrium with calcite at 25°C and 1 atm as a function of P_{CO_2} . From Drever (1988).

The solubility product of calcite is:

$$K_{\text{sp-cal}} = a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}} \quad 6.50$$

This can be combined with equations 6.21–23 to obtain the calcium concentration water in equilibrium with calcite as a function of P_{CO_2} :

$$[\text{Ca}^{2+}] = P_{\text{CO}_2} \frac{K_1 K_{\text{sp-cal}} K_{\text{sp-CO}_2}}{K_2 \gamma_{\text{Ca}^{2+}} \gamma_{\text{HCO}_3^-}^2 [\text{HCO}_3^-]^2} \quad 6.51$$

In a solution in equilibrium with calcite and a CO_2 gas phase and containing no other ions dissolved species, it is easy to modify equation 6.51 so that the calcium ion concentration is a function of P_{CO_2} only. A glance at Figure 6.1 shows that we can neglect OH^- , H^+ , and CO_3^{2-} if the final pH is less than about 9. The charge balance equation in this case reduces to:

$$2[\text{Ca}^{2+}] = [\text{HCO}_3^-] \quad 6.52$$

Substituting this into 6.51, we obtain:

$$[\text{Ca}^{2+}] = P_{\text{CO}_2} \frac{K_1 K_{\text{sp-cal}} K_{\text{sp-CO}_2}}{4 K_2 \gamma_{\text{Ca}^{2+}} \gamma_{\text{HCO}_3^-}^2 [\text{Ca}^{2+}]^2} \quad 6.53$$

$$\text{or } [\text{Ca}^{2+}] = \left[P_{\text{CO}_2} \frac{K_1 K_{\text{sp-cal}} K_{\text{sp-CO}_2}}{4 K_2 \gamma_{\text{Ca}^{2+}} \gamma_{\text{HCO}_3^-}^2} \right]^{1/3} \quad 6.54$$

There are two interesting aspects to this equation. First, the calcium ion concentration, and therefore calcite solubility, increases with increasing P_{CO_2} . This might at first seem counter-intuitive, as one might think that that increasing P_{CO_2} should produce an increase the carbonate ion concentration and therefore drive the reaction toward precipitation. However, increasing P_{CO_2} decreases pH, which decreases CO_3^{2-} concentration, and therefore drives the reaction towards dissolution. Second, calcium ion concentration varies with the one-third power of P_{CO_2} (Figure 6.11). Because of this non-linearity, mixing of two solutions, both of which are saturated

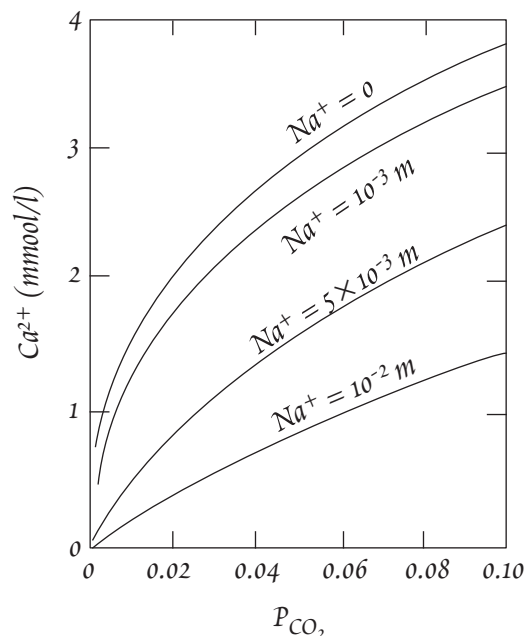


Figure 6.12. Concentration of calcium ion in a solution containing Na_2CO_3 in equilibrium with calcite at 25°C and 1 atm as a function of P_{CO_2} and sodium concentration. From Drever (1988).

CHAPTER 6: AQUATIC CHEMISTRY

in Ca^{2+} with respect to calcite, can result in the mixture being undersaturated with respect to Ca^{2+} . For example, consider the mixing of stream and ground water. Stream water is in equilibrium with the atmosphere for which P_{CO_2} is $10^{-3.5}$. On the other hand, P_{CO_2} in soils is often as high as 10^{-2} . So mixing between a calcite-saturated groundwater and a calcite-saturated surface water would produce a solution that is undersaturated with calcite.

Calcite solubility is also affected by the presence of other ions in solution. Figure 6.12 illustrates the effect of sodium ion concentration on calcite solubility.

Equation 6.54 describes calcite solubility for a system open to exchange with gaseous CO_2 . Water in pores and fractures in rocks does not exchange with a gas phase. Let's compare the open system with one that initially equilibrates with a P_{CO_2} of 10^{-2} and thereafter is closed to gas exchange, in other words, it has a fixed $\Sigma\text{CO}_{2\text{ initial}}$. We can write the following conservation equation for total carbonate:

$$\Sigma\text{CO}_2 = \Sigma\text{CO}_{2\text{ initial}} + \Sigma\text{CO}_{2\text{ from calcite}}$$

Since dissolution of one mole of calcite adds one mole of ΣCO_2 for each mole of Ca^{2+} , this equation may be rewritten as:

$$\Sigma\text{CO}_2 = \Sigma\text{CO}_{2\text{ initial}} + [\text{Ca}^{2+}]$$

Neglecting the contribution of the carbonate ion (*sensu stricto*) to total carbonate, this equation becomes:

$$[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] = ([\text{H}_2\text{CO}_3]_{\text{initial}}) + [\text{Ca}^{2+}] \quad 6.55$$

where $([\text{H}_2\text{CO}_3]_{\text{initial}})$ denotes that amount of H_2CO_3 calculated from equation 6.21 for equilibrium with CO_2 gas; in this case a partial pressure of 10^{-2} . This can be rearranged to obtain:

$$([\text{H}_2\text{CO}_3]_{\text{initial}}) = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] - [\text{Ca}^{2+}] \quad 6.56$$

Further constraints are provided by the three carbonate equilibrium product expressions (6.21–6.23) as well as the solubility product for calcite (6.50), and the charge balance equation. We assume a final pH less than 9 and no other ions present, so the charge balance equation reduces to equation 6.52. From equation 6.21 and the value of K_{CO_2} in Table 6.1, $[\text{H}_2\text{CO}_3]_{\text{initial}} = 10^{-2} \times 10^{-1.47}$ M. Dividing equation 6.22 by 6.23 yields:

$$\frac{K_1}{K_2} = \frac{[\text{HCO}_3^-]^2}{[\text{H}_2\text{CO}_3][\text{CO}_3^{2-}]}$$

Then substituting equations 6.53, 6.52, and 6.56 gives:

$$\frac{K_1}{K_2} = \frac{4[\text{Ca}^{2+}]^3}{K_{\text{sp-cal}}\{[\text{H}_2\text{CO}_3] - [\text{Ca}^{2+}]\}}$$

Finally, this is rearranged as:

$$[\text{Ca}^{2+}]^3 + \frac{K_1 K_{\text{cal}}}{4K_2} [\text{Ca}^{2+}] -$$

$$\frac{K_1 K_{\text{cal}} K_{\text{CO}_2}}{4K_2} (P_{\text{CO}_2\text{ initial}}) = 0 \quad 6.57$$

This yields a concentration of 3.34×10^{-4} m for the closed system case, which is 33.4 ppm of CaCO_3 since the molecular weight of CaCO_3 is 100.

By comparison, we can calculate from equation 6.54 that a solution open to exchange with a gas phase with P_{CO_2} will have a concentration of 139×10^{-3} m or 139 ppm CaCO_3 , over four times the con-

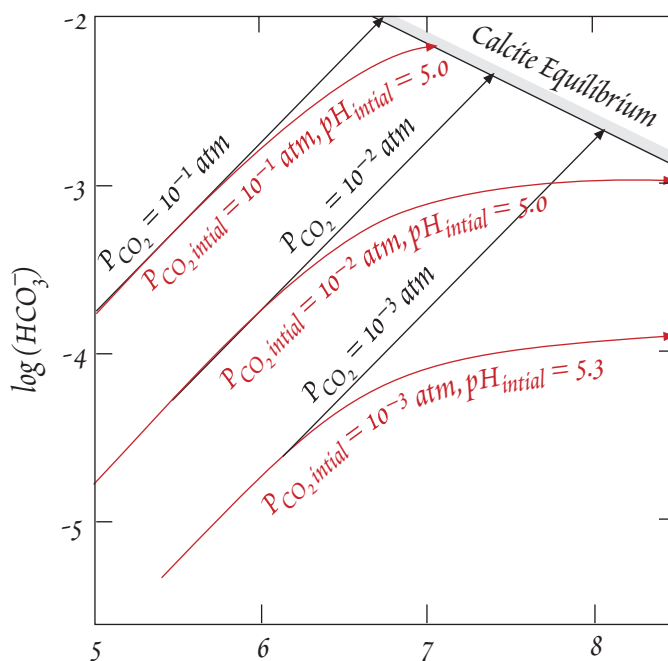


Figure 6.13. Comparison of the evolution of systems with constant P_{CO_2} (open systems) with those closed to gas exchange. After Stumm and Morgan (1981) and Deines et al. (1974).

CHAPTER 6: AQUATIC CHEMISTRY

centration in the closed system case. The difference is illustrated in Figure 6.13, which is a plot of $[\text{HCO}_3^-]$ vs. pH. Systems in equilibrium with constant P_{CO_2} (open systems) evolve along straight lines on this plot and ultimately reach calcite saturation at higher pH and lower $[\text{HCO}_3^-]$ (and $[\text{Ca}^{2+}]$) than closed systems that initially equilibrate with the same P_{CO_2} .

Solubility of Mg

There are a number of compounds that can precipitate from Mg-bearing aqueous solutions, including brucite ($\text{Mg}(\text{OH})_2$), magnesite (MgCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), as well as hydrated carbonates such as hydromagnesite ($\text{MgCO}_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$). The stability of these compounds may be described by the following reactions:



(The solubility of dolomite is poorly known; values for this equilibrium constant vary between $10^{-16.5}$ and 10^{-20} .)

We can use these reactions and their equilibrium constants, together with the reactions for the carbonate system (equ. 6.21-6.23) to construct predominance diagrams for Mg-bearing solutions in equilibrium with these phases. For example, for reaction 6.58, we may derive the following relationship (assuming ideal solution):

$$\log \frac{[\text{Mg}(\text{OH})_2]}{[\text{Mg}^{2+}]} = \text{p}K_{\text{bru}} - 2\text{p}K_{\text{w}} + 2\text{pH} = -16.4 + 2\text{pH} \quad 6.61$$

where we use the notation $\text{p}K = -\log(K)$. For reaction 6.59, we can derive the following:

$$\log \frac{[\text{MgCO}_3]}{[\text{Mg}^{2+}]} = \text{p}K_{\text{mag}} + \log \Sigma \text{CO}_2 + \frac{1}{[\text{H}^+]^2/K_1K_2 + [\text{H}^+]/K_2 + 1} \quad 6.62$$

Assuming the solid is a pure phase, the term on the left of each equation is then just $-\log[\text{Mg}^{2+}]$. We can use these equations to construct *stability*, or *predominance diagrams* in a manner similar to that used to construct pe-pH predominance diagrams (Chapter 4). For example, on a plot of $\log[\text{Mg}^{2+}]$ vs. pH, the predominance boundary between $\text{Mg}_{\text{aq}}^{2+}$ and brucite plots as a line with a slope of -2 and an intercept of $+16.4$. Figure 6.14 shows two predominance diagrams derived from these equations. Brucite is the stable phase at high pH and low P_{CO_2} .

Virtually all natural solutions will contain dissolved calcium as well as magnesium. This being the case, we must also consider the stability of dolomite. We can construct similar predominance dia-

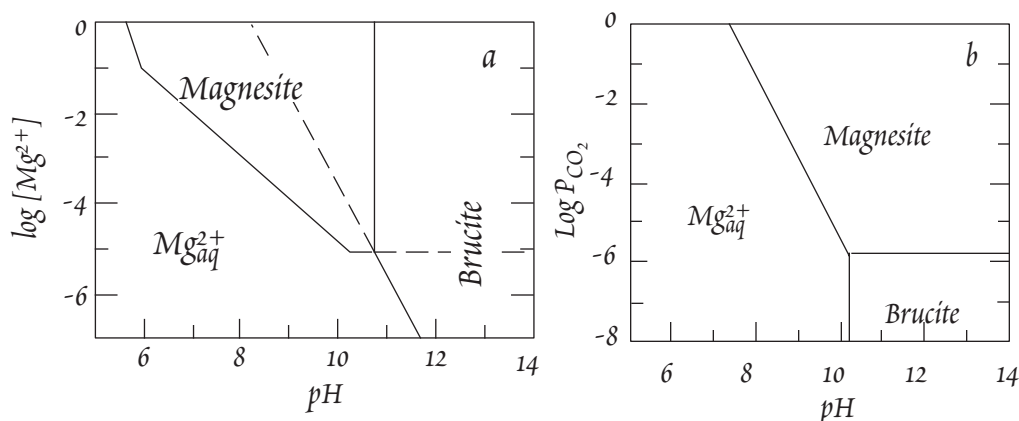
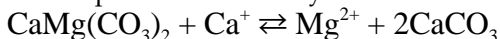


Figure 6.14. Predominance diagrams for Mg-bearing phases in equilibrium with aqueous solution. The concentration of Mg^{2+} is set at 10^{-4}M in 6.14b.

CHAPTER 6: AQUATIC CHEMISTRY

grams for these systems but we must add an additional variable, namely the Ca^{2+} concentration. To describe the relative stability of dolomite and calcite, it is more convenient to express the solubility of dolomite as:



because the reaction contains calcite as well as dolomite. Since this reaction can be constructed by subtracting 2 times the calcite dissolution (equ. 6.50) from the dolomite dissolution (6.60), the equilibrium constant for this reaction can be calculated from:

$$K = \frac{K_{\text{dol}}}{K_{\text{cal}}^2}$$

Figure 6.15 illustrates the stability of magnesite, dolomite, brucite and calcite as a function of P_{CO_2} and the $\text{Ca}^{2+}/\text{Mg}^{2+}$ concentration ratio. Whether any of these phases are stable relative to a Mg^{2+} -bearing solution depends on the Mg^{2+} concentration, which is not specified in the graph.

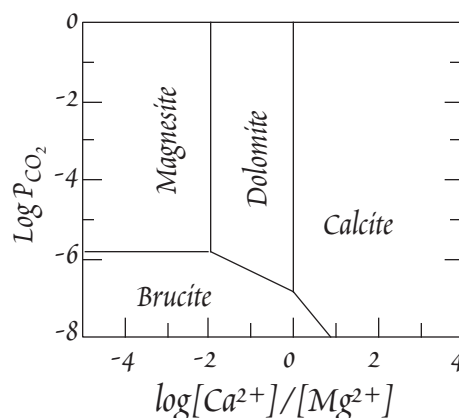
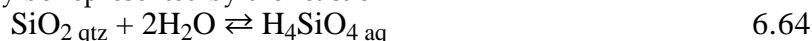


Figure 6.15. Stability of magnesite, dolomite, calcite, and brucite in equilibrium with a Mg- and Ca-bearing aqueous solution.

Solubility of SiO_2

Silicon is the most common elements on the Earth's surface after oxygen. Its concentration in solution plays an important role in determining how weathering will proceed.

The dissolution of silica may be represented by the reaction:

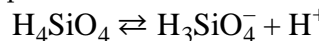


The equilibrium constant expression is simply:

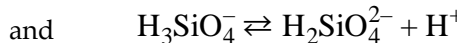
$$K_{\text{qtz}} = a_{\text{H}_4\text{SiO}_4} = 10^{-4} \text{ at } 25^\circ\text{C} \quad 6.65$$

This is to say, water is saturated with respect to quartz when the concentration of H_2SiO_4 is 10^{-4} moles per kilogram, which corresponds to about 7.8 ppm by weight SiO_2 .

However, there are some complicating factors. First, precipitation of quartz seems to be strongly kinetically inhibited. Equilibrium is more likely to be achieved with amorphous silica, the equilibrium constant for which is 2×10^{-3} (~115 ppm). Second, H_4SiO_4 is a weak acid and undergoes successive dissociation with increasing pH:



$$K_1 = \frac{a_{\text{H}_3\text{SiO}_4^-} a_{\text{H}^+}}{a_{\text{H}_4\text{SiO}_4}} = 10^{-9.9}$$



$$K_2 = \frac{a_{\text{H}_2\text{SiO}_4^{2-}} a_{\text{H}^+}}{a_{\text{H}_3\text{SiO}_4^-}} = 10^{-11.7}$$

The total dissolved silica concentration will be the sum of H_4SiO_4 , H_3SiO_4^- , and $\text{H}_2\text{SiO}_4^{2-}$. Assuming activity coefficients of unity, the concentration of dissolved silica is then:

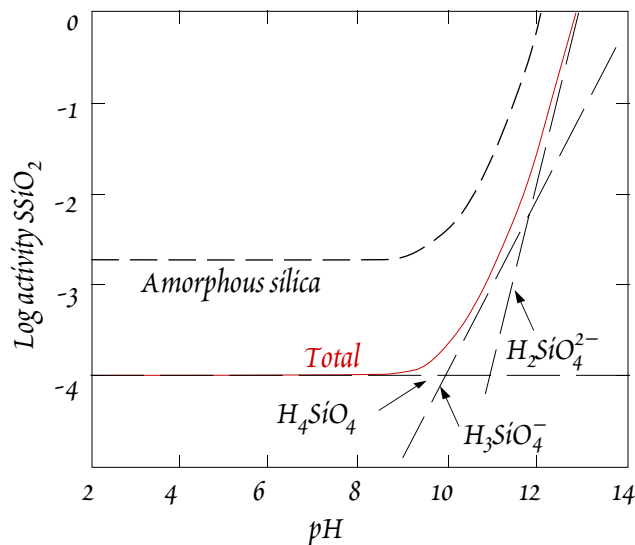


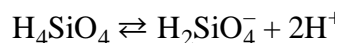
Figure 6.16. Log activity of dissolved silica in equilibrium with quartz and amorphous silica (dashed line) as a function of pH. After Drever (1988).

CHAPTER 6: AQUATIC CHEMISTRY

$$[\text{SiO}_2]_{\text{T}} = [\text{H}_2\text{SiO}_4] \left\{ 1 + \frac{K_1}{a_{\text{H}^+}} + \frac{K_1 K_2}{a_{\text{H}^+}^2} \right\} \quad 6.66$$

From equation 6.66, we would expect silica solubility to be pH dependent. This dependence is illustrated in Figure 6.16.

We could have defined the second dissociation reaction as:



In which case, the equilibrium constant would be:

$$K_2^* = \frac{a_{\text{H}_2\text{SiO}_4^{2-}} a_{\text{H}^+}^2}{a_{\text{H}_4\text{SiO}_4}} = 10^{-11.7} \times 10^{-9.9}$$

and equation 6.66 would have been:

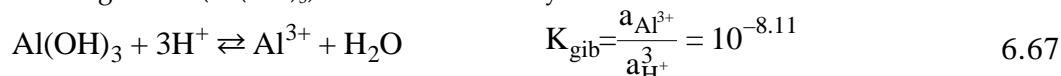
$$[\text{SiO}_2]_{\text{T}} = [\text{H}_2\text{SiO}_4] \left\{ 1 + \frac{K_1}{a_{\text{H}^+}} + \frac{K_2^*}{a_{\text{H}^+}^2} \right\} \quad 6.66a$$

The concentration of $\text{SiO}_{2\text{T}}$ we calculate in this way would, of course, be identical. The point is, reactions and their corresponding equilibrium constants can be expressed in various ways, and we need to be alert to this.

Solubility of $\text{Al}(\text{OH})_3$ AND OTHER HYDROXIDES

The hydroxide is the least soluble salt of many metals. Therefore, it is the solubility of the metal hydroxides that controls the solubility of these metals in natural waters. These are shown in Figure 6.17. Since these dissolution reactions involve OH^- , they are pH dependent, and the slope of the solubility curve depends on the valence of the metal (e.g., -3 for Fe^{3+} , -2 for Fe^{2+} , -1 for Ag^{3+}). Let's consider in more detail the solubility of gibbsite, the hydroxide of aluminum.

Dissolution of gibbsite ($\text{Al}(\text{OH})_3$) can be described by the reaction:



However, a complication arises from hydrolyzation of the aluminum, which occurs in solutions that are not highly acidic (hydrolyzation is typical of many of the highly charged, ≥ 3 , metal ions):

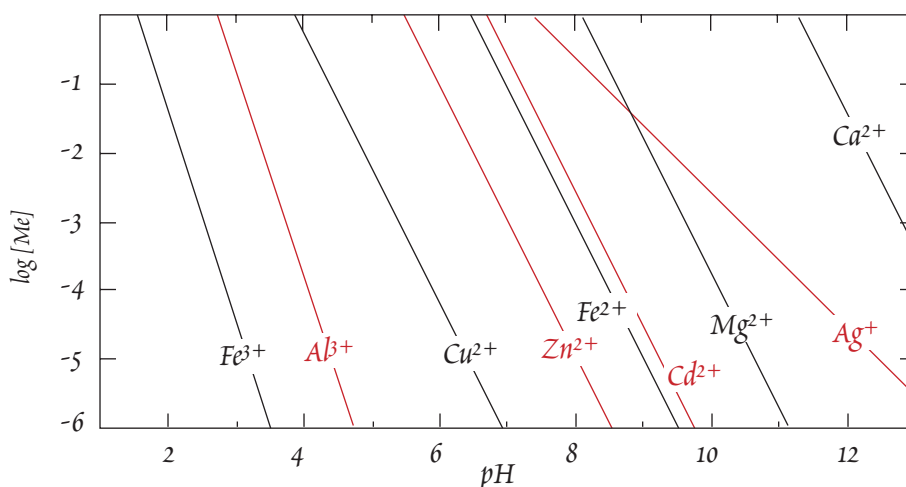


Figure 6.17. Solubility of metal hydroxides as a function of pH. After Stumm and Morgan (1981).

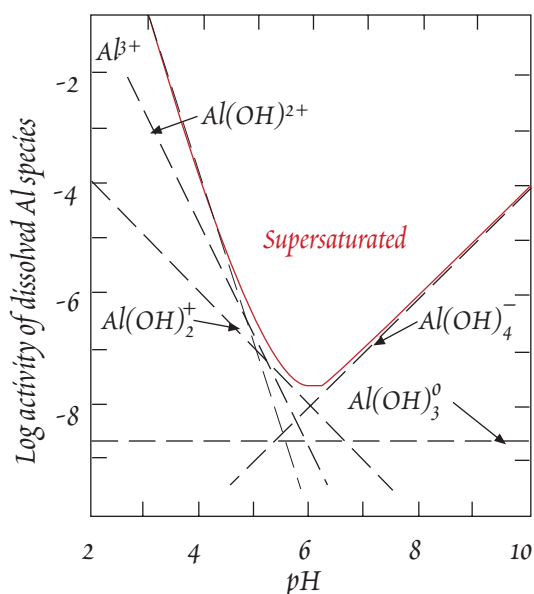


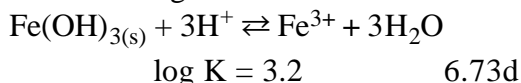
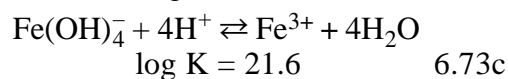
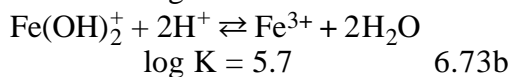
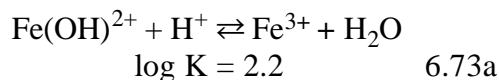
Figure 6.18. Log activity of dissolved aluminum species and total Al (solid red line) in equilibrium with gibbsite as a function of pH.

Figure 6.18 shows the concentrations of the various aluminum species and total aluminum as a function of pH. The solubility of Al is low except at low and high pH, and that as pH increases Al^{3+} becomes increasingly hydrolyzed. Also note that where positively charged species dominate, e.g., Al^{3+} , solubility increases with decreasing pH; where negatively charged species dominate, solubility increases with increasing pH. Minimum solubility occurs in the range of pH of natural waters (which is just as well because it has some toxicity).

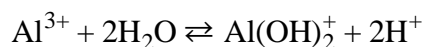
Equation 6.72 is a general result that can be applied to metals other than those that undergo hydrolyzation reactions, when the reactions are expressed in the same form as those above. A general form of this equation would thus be:

$$[\text{M}]_{\text{T}} = [\text{M}^{\text{Z}}] \left\{ 1 + \frac{K_1}{a_{\text{H}^+}} + \frac{K_2}{a_{\text{H}^+}^2} + \frac{K_3}{a_{\text{H}^+}^3} + \dots \right\} \quad 6.73$$

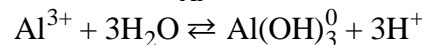
Thus iron and other metals show a pH dependence similar to Al. For Fe, the relevant equilibrium constants are:



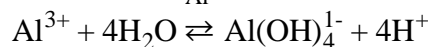
Using these equilibrium constants, the solubility of amorphous goethite as a function of pH is readily calculated and is shown in Figure 6.19.



$$K_2 = \frac{a_{\text{Al}(\text{OH})_2^+} a_{\text{H}^+}^2}{a_{\text{Al}^{3+}}} = 10^{-9.3} \quad 6.69$$



$$K_3 = \frac{a_{\text{Al}(\text{OH})_3^0} a_{\text{H}^+}^3}{a_{\text{Al}^{3+}}} = 10^{-16} \quad 6.70$$



$$K_4 = \frac{a_{\text{Al}(\text{OH})_4^-} a_{\text{H}^+}^4}{a_{\text{Al}^{3+}}} = 10^{-22} \quad 6.71$$

Neglecting activity coefficients, the total dissolved aluminum concentration is given by:

$$[\text{Al}]_{\text{T}} = [\text{Al}^{3+}] \left\{ 1 + \frac{K_1}{a_{\text{H}^+}} + \frac{K_2}{a_{\text{H}^+}^2} + \frac{K_3}{a_{\text{H}^+}^3} + \frac{K_4}{a_{\text{H}^+}^4} \right\} \quad 6.72$$

Figure 6.18 shows the concentrations of the various aluminum species and total aluminum as a function of pH. The solubility of Al is low except at low and high pH, and that as pH increases Al^{3+} becomes increasingly hydrolyzed. Also note that where positively charged species dominate, e.g., Al^{3+} , solubility increases with decreasing pH; where negatively charged species dominate, solubility increases with increasing pH. Minimum solubility occurs in the range of pH of natural waters (which is just as well because it has some toxicity).

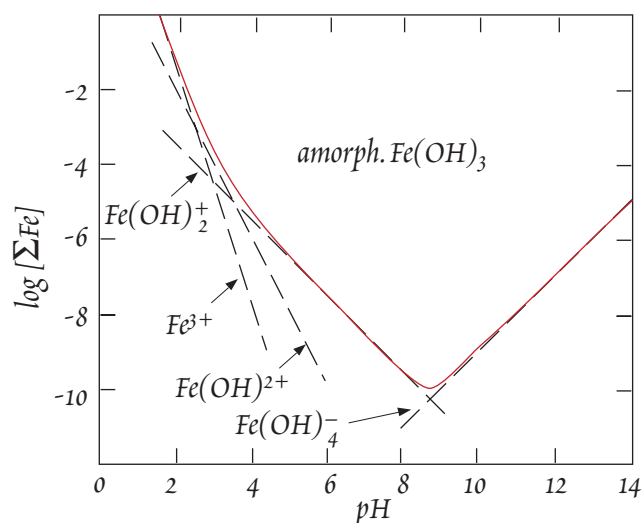
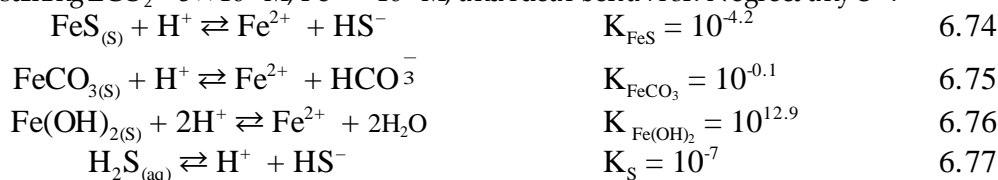


Figure 6.19. Solubility of goethite as a function of pH. Solubility of individual Fe-hydroxide species shown as dashed lines.

EXAMPLE 6.8. CONSTRUCTING STABILITY DIAGRAMS

Using the equilibrium constant data below as well as from Table 6.1, construct a stability diagram showing the stability of FeS, siderite (FeCO_3), and $\text{Fe}(\text{OH})_2$ as a function of total sulfide concentration and pH assuming $\Sigma\text{CO}_2 = 5 \times 10^{-2} \text{ M}$, $\text{Fe}^{2+} = 10^{-6} \text{ M}$, and ideal behavior. Neglect any S^{2-} .



Answer: Our first step is to set up an equation that describes the concentration of HS^- as a function of pH. From the conservation of sulfur, we have:

$$\Sigma\text{S} = [\text{H}_2\text{S}] + [\text{HS}^-]$$

From the equilibrium constant expression for the dissociation of H_2S , we may substitute:

$$[\text{H}_2\text{S}] = \frac{[\text{H}^+][\text{HS}^-]}{K_s} \quad \text{and obtain:} \quad \Sigma\text{S} = \frac{[\text{H}^+][\text{HS}^-]}{K_s} + [\text{HS}^-] \quad 6.78$$

$$[\text{HS}^-] = \Sigma\text{S} \frac{K_s}{K_s + [\text{H}^+]}$$

Solving for $[\text{HS}^-]$ we have:

We substitute this into the FeS solubility product and solving for ΣS we have:

$$\Sigma\text{S} = \frac{K_{\text{FeS}}[\text{H}^+](K_s + [\text{H}^+])}{[\text{Fe}^{2+}] K_s} \quad 6.79$$

or in log form: $\log(\Sigma\text{S}) = \log(K_s + [\text{H}^+]) - \text{pH} - \log([\text{Fe}^{2+}]) + \text{p}K_{\text{FeS}} - \text{p}K_s$

This plots as line ① on our ΣS vs. pH stability diagram (Figure 6.20). The area above the line is the region where FeS is stable.

Next we need an equation describing the concentration of HCO_3^- as a function of pH, which is equation 6.29. Substituting this into the siderite solubility product we have:

$$K_{\text{FeCO}_3} = \frac{[\text{Fe}^{2+}]\Sigma\text{CO}_2}{\left\{ \frac{[\text{H}^+]}{K_1} + 1 + \frac{K_2}{[\text{H}^+]} \right\} [\text{H}^+]}$$

or in log form:

$$0 = \text{pH} + \log[\text{Fe}^{2+}] + \log\Sigma\text{CO}_2 - \log\left\{ \frac{[\text{H}^+]}{K_1} + 1 + \frac{K_2}{[\text{H}^+]} \right\} - \text{p}K_{\text{FeCO}_3} \quad 6.80$$

An approximate solution may be found by assuming $\text{HCO}_3^- = \Sigma\text{CO}_2$, which yields $\text{pH} = 8.20$. An exact solution requires an indirect method. Using the Solver in Microsoft Excel™, we find obtain $\text{pH} = 8.21$, very close to our approximate solution (Solver uses a succession of “intelligent” guesses to find solutions to equations, such as 6.80, that have no direction solution). Thus siderite will precipitate when the pH is greater than 8.21 and, not surprisingly, this is independent of ΣS . The boundary between the Fe^{2+} and FeCO_3 field is then a vertical line (line ②) at $\text{pH} = 8.21$.

The condition for precipitation of $\text{Fe}(\text{OH})_2$ is described by the equation:

$$\text{pH} = \frac{\text{p}K_{\text{Fe}(\text{OH})_2} - \log[\text{Fe}^{2+}]}{2} = 9.45 \quad 6.81$$

Thus $\text{Fe}(\text{OH})_2$ will not precipitate until pH reaches 9.5, i.e., above the point where FeCO_3 precipitates, so there is no boundary between a $\text{Fe}(\text{OH})_2$ phase and a Fe^{2+} -bearing solution.

Next we need equations that describe the reactions between solid phases. A reaction between FeCO_3 and $\text{Fe}(\text{OH})_2$ can be obtained by subtracting reaction 6.76 from reaction 6.75. The corresponding equilibrium constant is obtained by dividing 6.75 by 6.76:



CHAPTER 6: AQUATIC CHEMISTRY

From this we derive: $\text{pH} = \log [\text{HCO}_3^-] + 13.02$ 6.82

Substituting equation 6.15 for HCO_3^- we can obtain an approximate solution assuming $\text{HCO}_3^- = \Sigma\text{CO}_2$, which yields $\text{pH} = 10.72$. An exact solution using the Solver in Excel™ yields $\text{pH} = 10.5$. Not surprisingly, our approximate solution is less accurate than in the previous case because at this high pH, the carbonate ion makes up a substantial fraction of the total carbonate (Figure 6.1). The boundary between the FeCO_3 and $\text{Fe}(\text{OH})_2$ fields is thus a vertical line at $\text{pH} = 10.5$ (line ③).

The boundary between FeS and FeCO_3 is found by subtracting reaction 6.75 from 6.74 and dividing the corresponding equilibrium constants:



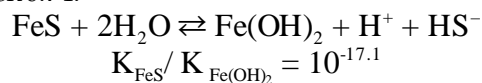
Substituting 6.78 and 6.15 into the corresponding equilibrium constant expression, we have:

$$\begin{aligned} \log[\text{HS}^-] - \log[\text{HCO}_3^-] &= \\ \log\Sigma\text{S} + \text{p}K_{\text{S}} - \log(K_{\text{S}} + [\text{H}^+]) &= \\ -\log\Sigma\text{CO}_2 + \log\left\{\frac{[\text{H}^+]}{K_1} + 1 + \frac{K_2}{[\text{H}^+]}\right\} &= -4.1 \end{aligned}$$

Solving for ΣS , we have:

$$\begin{aligned} \log\Sigma\text{S} &= -\text{p}K_{\text{S}} + \log(K_{\text{S}} + [\text{H}^+]) + \\ \log\Sigma\text{CO}_2 - \log\left\{\frac{[\text{H}^+]}{K_1} + 1 + \frac{K_2}{[\text{H}^+]}\right\} &- 4.1 \end{aligned}$$

This plots as line ④ on our diagram. Finally, the reaction between FeS and $\text{Fe}(\text{OH})_2$ is obtained by subtracting reaction 6.76 from reaction 6.74:



From the equilibrium constant equation we obtain an expression of ΣS as a function of pH:

$$\log\Sigma\text{S} = \text{pH} - \text{p}K_{\text{S}} + \log(K_{\text{S}} + [\text{H}^+]) - 17.1$$

This plots as line ⑤ on our diagram, which is now complete.

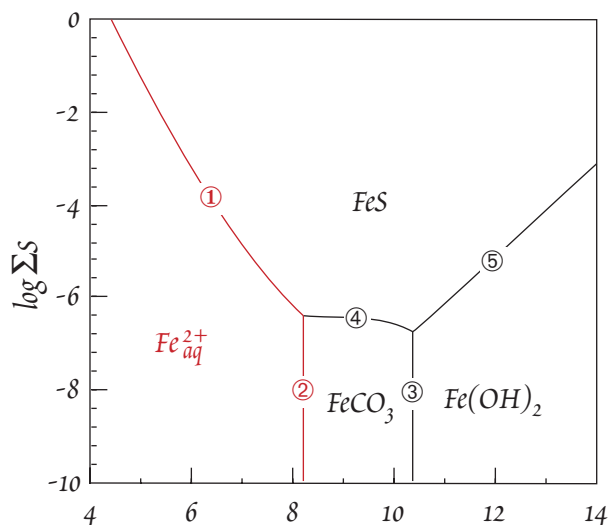
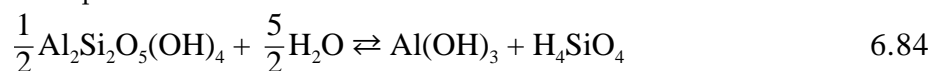


Figure 6.20. Stability diagram showing the stable solid Fe-bearing phases in equilibrium with a solution containing 10^{-6} M Fe^{2+} and 5×10^{-3} M ΣCO_2 .

Dissolution of Silicates and Related Minerals

The concentrations of Al and Si will usually not be controlled by equilibrium with quartz and gibbsite, rather by equilibrium with other silicates. An example of this is shown in Figure 6.21, which shows the concentration of dissolved Al in equilibrium with gibbsite, kaolinite and pyrophyllite at four different activities of dissolved silica. Only at the lowest dissolved silica concentrations will gibbsite precipitate before one of the aluminosilicates.

For the most part, silicates do not dissolve in the conventional sense, rather they react with water to release some ions to solution and form new minerals in place of the original ones. This phenomenon is known as *incongruent solution*. In considering such reactions, we can usually assume all Al remains in the solid phase. If we consider only Al and Si, a simple reaction might be the breakdown of kaolinite to form gibbsite plus dissolved silica:



Since the solid phases can be viewed as pure, the equilibrium constant for this reaction is simply:

$$K = a_{\text{H}_4\text{SiO}_4} = 10^{-4.4} \quad 6.85$$

CHAPTER 6: AQUATIC CHEMISTRY

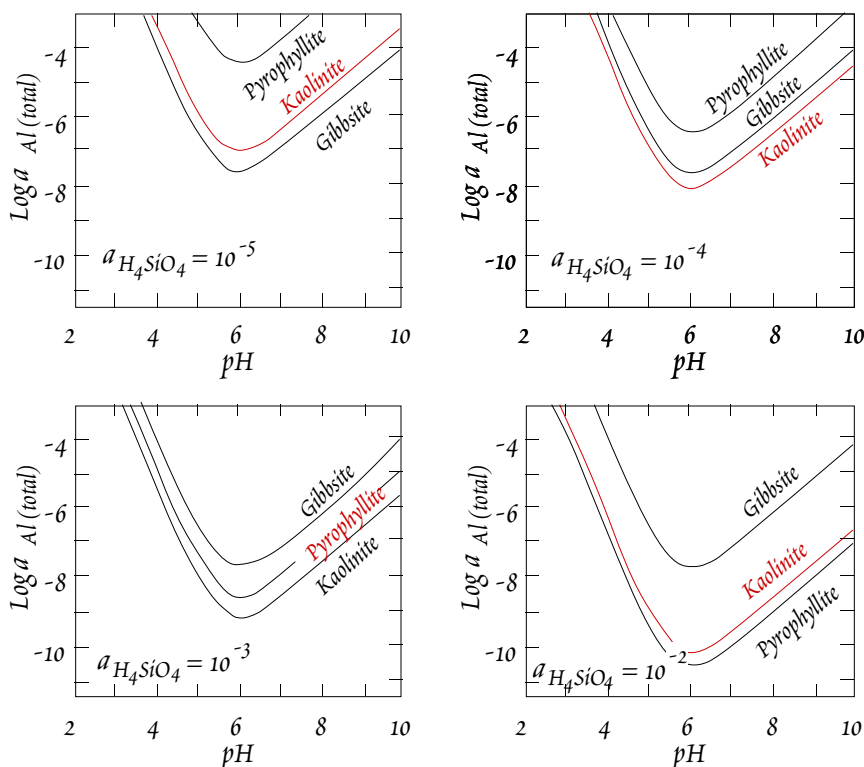
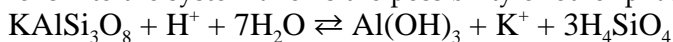


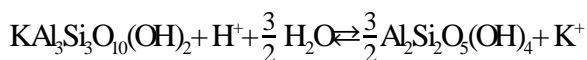
Figure 6.21. Total dissolved Al activity in equilibrium with gibbsite, pyrophyllite, and kaolinite as a function of pH at different dissolved silica activities. After Drever (1988).

which tells us that at H_2SiO_4 activities greater than $10^{-4.4}$, kaolinite is more stable than gibbsite. Similar reactions can, of course, be written between other phases, such as kaolinite and pyrophyllite. Introducing other ions into the system allows the possibility of other phases and other reactions, e.g.:



$$K = \frac{a_{K^+} a_{H_4SiO_4}}{a_{H^+}} \quad 6.86$$

and:



$$K_{\text{mus-kao}} = \frac{a_{K^+}}{a_{H^+}} \quad 6.87$$

From a series of such reactions and their corresponding equilibrium constant expressions, we can construct stability diagrams such as the one in Figure 6.22. The procedure for constructing this and similar diagrams is essentially similar to that used in construction of pE–pH diagrams and is illustrated in Example 6.8. In the case of Figure 6.22, we seek an equilibrium constant expression containing the a_{K^+}/a_{H^+} ratio and the activity of H_4SiO_4 . From this expression we determine the slope and intercept, which allows us to plot the predominance boundary. For example, the boundary between the kaolinite and

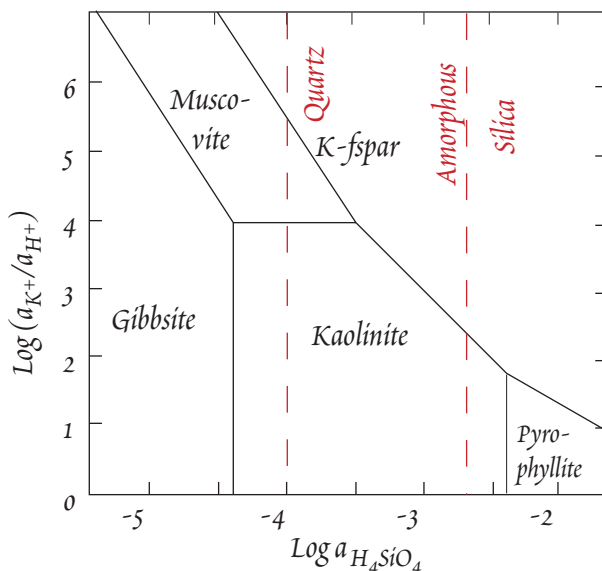
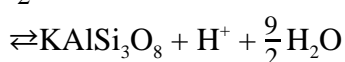
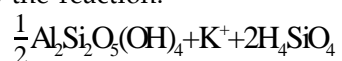


Figure 6.22. Stability diagram for the system $K_2O-Al_2O_3-SiO_2-H_2O$ at 25°C. After Drever (1988).

CHAPTER 6: AQUATIC CHEMISTRY

muscovite fields is given by equation 6.87. The equilibrium constant for the reaction is 10^4 , so the boundary is a line with slope 0 at $\log a_{K^+}/a_{H^+} = 4$. The boundary between gibbsite and kaolinite is reaction 6.84, and equation 6.85, written in log form, defines the line dividing the two regions. This boundary thus plots as a vertical line at $\log a_{H_4SiO_4} = -4.4$. The kaolinite – K-feldspar boundary is the reaction:



$$K_{ka-kf} = \frac{a_{H^+}}{a_{K^+} a_{H_2SO_4}^2}$$

$$\log \frac{a_{K^+}}{a_{H^+}} = -\log K - 2\log a_{H_2SO_4}$$

The boundary thus plots as a line with a slope of -2 and an intercept equal to the negative of the log of the equilibrium constant. Boundaries for the remaining fields can be derived similarly.

The fields in Figure 6.22 show the phase that is the most stable of those we considered in constructing the diagram. (Strictly speaking, it does not tell us whether the phase can be expected to precipitate or not, as this depends on the Al activity; however, because of the low solubility of Al, an aluminum-bearing phase can be expected to be stable in most instances.) By considering sodium and calcium as well as potassium, we can construct a 3-dimensional stability diagram, such as that in Figure 6.23, in a similar manner.

Because many low-temperature reactions involving silicates are so sluggish, equilibrium constants are generally calculated from thermodynamic data rather than measured.

CLAYS AND THEIR PROPERTIES

Clays are ubiquitous on the surface of the Earth. Unfortunately, the term *clay* has two meanings in geology: in a mineralogical sense it refers to a group of sheet silicates, in another sense it refers to the finest fraction of a sediment or soil. In addition to clay minerals, fine-grained oxides and hydroxides are present in the 'clay fraction'. Clays, in both senses, exert important controls on the composition of aqueous fluids, both because of chemical reactions that form them and because of their sorptive and ion exchange capacities. Generally, only clays in the mineralogical sense have true ion-exchange capacity, where ions in the clay can be exchanged for ions in the surrounding solution, but oxides and hydroxides can adsorb and desorb ions on their surfaces. We will first consider the mineralogy of the true clays, then consider their interaction with solution.

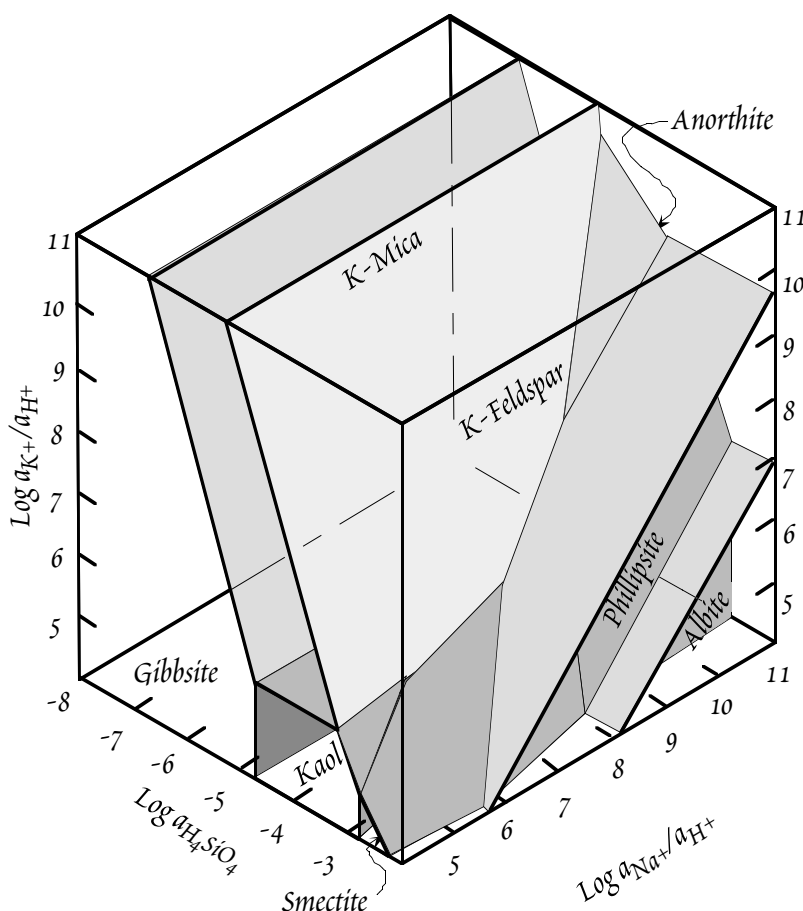


Figure 6.23. Stability diagram for the system $K_2O-Na_2O-CaO-Al_2O_3-SiO_2-H_2O$ at $25^\circ C$. After Drever (1988).

CHAPTER 6: AQUATIC CHEMISTRY

CLAY MINERALOGY

Clay minerals (*sensu stricto*) are sheet silicates. We can think of each sheet in a clay mineral as consisting of layers of silica tetrahedra bound to a hydroxide layer in which the cation (most commonly Al, Mg, or Fe) is in octahedral coordination much as in pure hydroxide minerals such as gibbsite ($\text{Al}(\text{OH})_3$) or brucite ($\text{Mg}(\text{OH})_2$). Brucite and gibbsite are structurally similar to each other except that in gibbsite every third octahedral site is left empty to maintain charge balance. This is illustrated in Figure 6.24. Because only 2 out of 3 octahedral sites are occupied, gibbsite is said to have a *dioctahedral* structure, while brucite is said to be *trioctahedral*. This terminology also applies in clay minerals in exactly the same sense.

KAOLINITE GROUP (1:1 CLAYS)

The simplest clays consist of a tetrahedral silicate layer and an octahedral hydroxide layer, hence the term 1:1 clays.

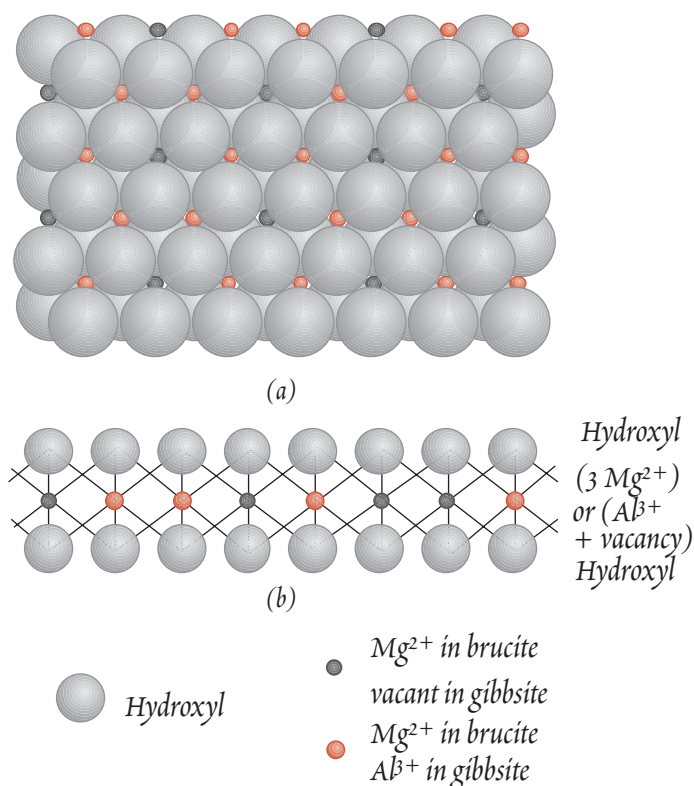


Figure 6.24. Structure of gibbsite and brucite. (a) plan (vertical) view; (b) expanded x-sectional view.

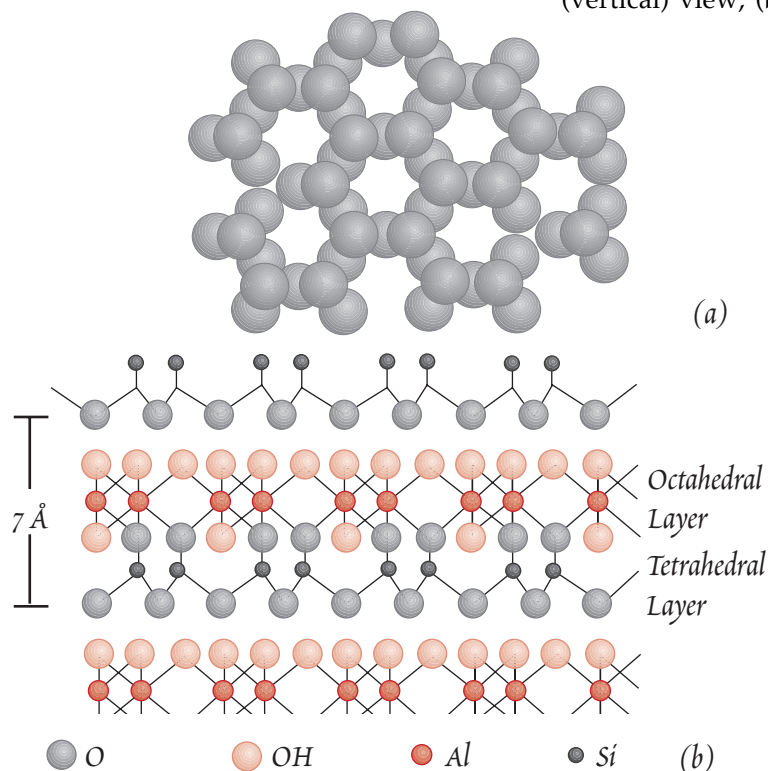


Figure 6.25. Structure of kaolinite. (a) Plan view of the tetrahedral layer. (b) Cross-sectional view.

Kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, is a good example. The structure of kaolinite is shown in Figure 6.25. Its unit cell consists of a layer of silica tetrahedra bound to an octahedral alumina layer whose structure is very similar to that of gibbsite except that some oxygens are replaced by hydroxyls. Note that individual sheets are not bound together; they are held together only by van der Waals interactions, which are quite weak. The structure of serpentine, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, is similar to that of kaolinite, with Mg replacing Al, and every octahedral site is occupied. In both minerals, a mismatch in the spacing of octahedra and tetrahedra results in a curvature of the lattice. Also successive layers of kaolinite are generally stacked in a random manner.

CHAPTER 6: AQUATIC CHEMISTRY

Pyrophyllite Group (2:1 Clays)

This is a large group of clay minerals consisting of a "hydroxide layer" sandwiched between two layers of silica tetrahedra, hence the term 2:1 clays. More of the hydroxyls in the hydroxide layer are replaced by oxygen than in 1:1 clays. The simplest two such clays are pyrophyllite, $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$, and talc, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$. In pyrophyllite, every third octahedral site is vacant, so that it, like kaolinite, is said to be dioctahedral, while serpentine and talc are trioctahedral. The structure of pyrophyllite is shown in Figure 6.26. Other, more complex clays, including those of the smectite group, the biotite group, the vermiculite group, saponite, and muscovite, have structures similar to those of pyrophyllite and talc. These are derived in the following ways (Figure 6.27):

1. Substitution of Al^{+3} for Si^{+4} in the tetrahedral sites resulting in a charge deficiency that is balanced by the presence of a cation between the layers (interlayer positions). When the number of interlayer cations is small, they are generally exchangeable; when the number is large, K is typically the cation and it is not very exchangeable.
2. Substitution of Mg^{2+} , Fe^{2+} , Fe^{3+} or a similar cation for Al^{3+} or substitution of Fe^{2+} , Fe^{3+} , or Al^{3+} for Mg^{2+} in the octahedral layer. Where charge deficiency results, it is balanced by the presence of exchangeable cations in the interlayer sites, or by vacancies in the octahedral sites.

Smectites are distinguished by their expansion to a unit cell thickness of 14 Å upon treatment with ethylene glycol. This expansion results from entry of the

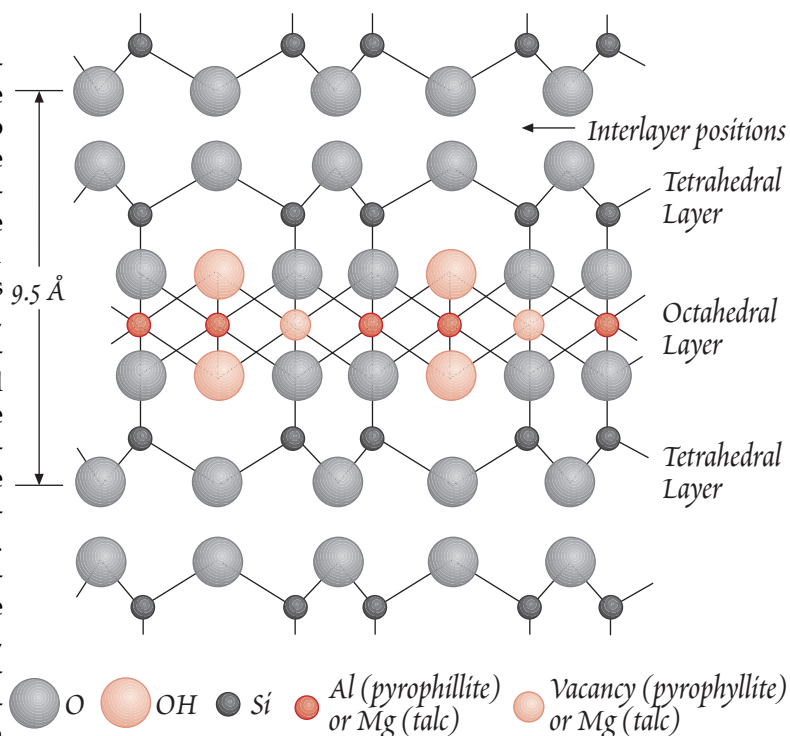
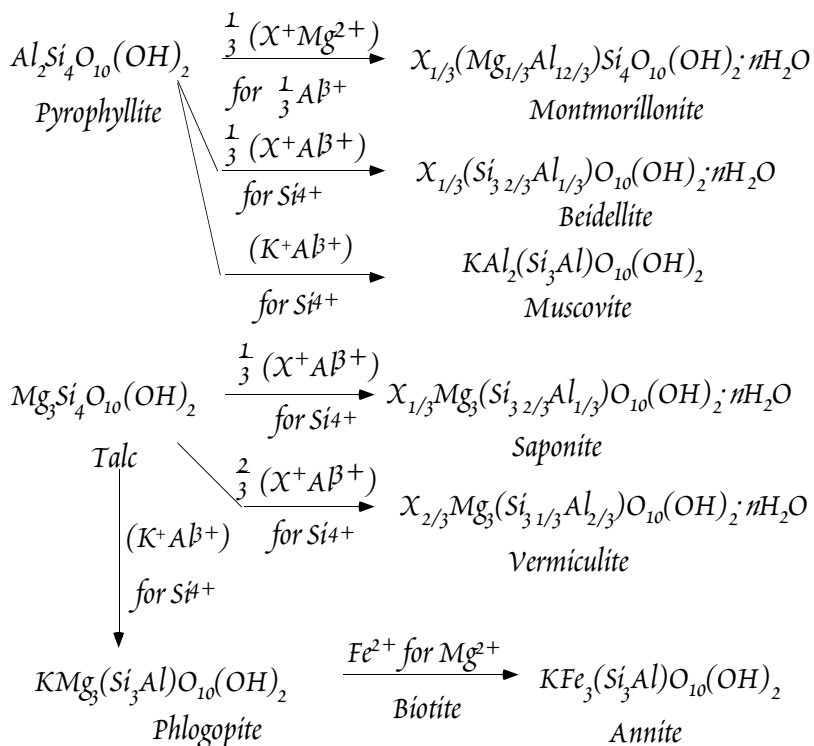


Figure 6.26. Structure of pyrophyllite.

Figure 6.27. Relationship of 2:1 clays to pyrophyllite and talc. X represents an exchangeable cation (K, Na, $\frac{1}{2}$ Mg, $\frac{1}{2}$ Ca, etc.). From Drever (1988).

CHAPTER 6: AQUATIC CHEMISTRY

ethylene glycol molecule into the interlayer position of the clays. Smectites generally also have water present in the interlayer space, the amount of water being determined by the cation present. Generally there is little water present when the interlayer cation is divalent Mg or Ca, but can be very considerable when the cation is Na. The amount of water also depends on the humidity; as a result smectites, and sodium bearing ones in particular will swell on contact with water, affecting permeability. The most common smectite is montmorillonite, $X_{1/3}(Mg_{1/3}Al_{5/3})Si_4O_{10}(OH)_2 \cdot nH_2O$. The interlayer cation of smectites is exchangeable: in a NaCl solution it will be Na, in a $CaCl_2$ solution it will be Ca, etc.

Vermiculites have a higher net charge on the 2:1 layer (that is, there is greater cation deficiency). As a result, the electrostatic forces holding the layers together are greater so that the interlayer space is less expandable and the interlayer cations less exchangeable.

Micas (biotite and muscovite) are related to pyrophyllite and talc by substitution of an Al^{3+} for a Si^{4+} in a tetrahedral site. The result is that the silicate layers are relatively strongly bound to the interlayer K, which is not normally exchangeable. *Illite* is a name applied to clay-sized micas, though it is sometimes restricted to the dioctahedral mica (muscovite). Generally, illite has less K and Al and more Si than igneous or metamorphic muscovite.

Because of the structural similarity of various 2:1 clays, they can form crystals that consist of layers of more than one type, for example illite-smectite. In addition, layers of gibbsite or brucite may occur in smectite. Different layers may be distributed randomly or may be ordered. These are called, for example, mixed-layer chlorite-smectite or hydroxy-interlayer smectite.

Chlorite Group (2:2 clays)

This group is characterized by having a unit cell consisting of two tetrahedral layers and two (hydroxide) octahedral layers. The ideal formula of chlorite is $(Mg,Fe,Al)_6(SiAl)_4O_{10}(OH)_8$, where the elements in parentheses can be in any proportions. The structure of chlorite is shown in Figure 6.28. Chlorites with unit cells consisting of a single tetrahedral and single octahedral layer also occur and are called septecklorite (because they have a 7Å spacing; true chlorites have 14Å spacing), but are less stable and uncommon.

ION-EXCHANGE PROPERTIES OF CLAYS

One of the most important properties of clays is their capacity for ion exchange. In soil science, the term *ion exchange* is refers specifically to replacement of an ion adsorbed to the surface by one in solution. However, we shall use the term in a more general sense here, and include as well exchange reactions between ions in solution and ions bound within the solid. The ability of a substance to exchange ions is called the *ion exchange capacity* and is generally measured in equivalents or milliequivalents (meq). Ion exchange capacities of clays are listed in Table 6.3.

The exchange reaction of two monovalent ions between clay

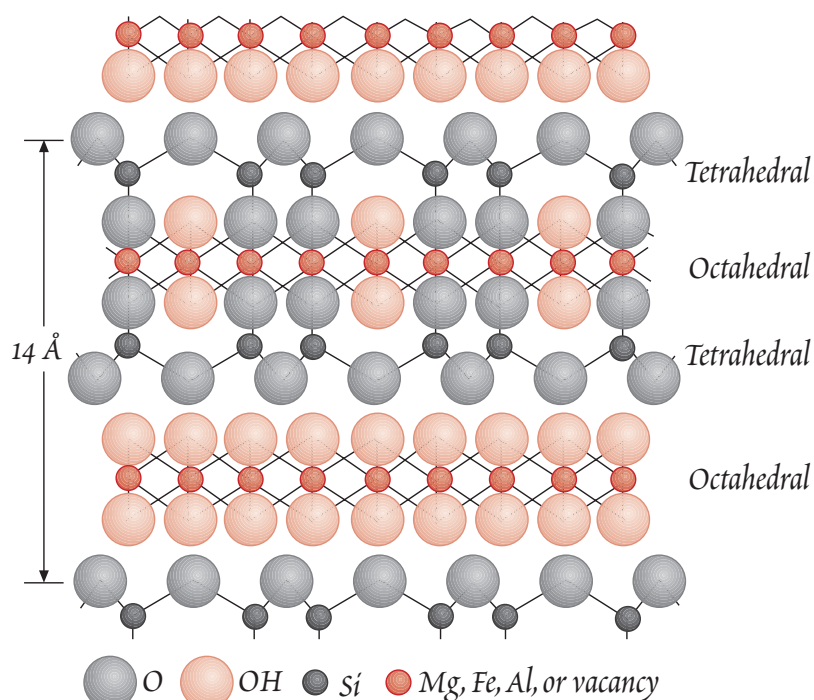
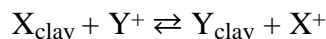


Figure 6.28. Structure of Chlorite.

CHAPTER 6: AQUATIC CHEMISTRY

and solution may be written:



The corresponding equilibrium constant expression is written as:

$$\frac{a_{Y\text{-clay}}a_{X^+}}{a_{X\text{-clay}}a_{Y^+}} = K \quad \text{or:} \quad \frac{a_{Y\text{-clay}}}{a_{X\text{-clay}}} = K \frac{a_{Y^+}}{a_{X^+}} \quad 6.88$$

If we express this with molar concentrations in solution and mole fractions (X) in the solid rather than activities:

$$\frac{X_{Y\text{-clay}}}{X_{X\text{-clay}}} = K'_{YX} \frac{[Y^+]}{[X^+]}$$

K' is called the *selectivity constant*. It expresses the selectivity of the clay for the Y ion over the X ion. Because we have expressed it in mole fraction rather than activity, we can expect its value to depend on the composition of both the clay and the solution. We may also define a *distribution coefficient*, K_d as:

$$K_d = \frac{[X_{\text{clay}}]}{[X^+]} \quad 6.89$$

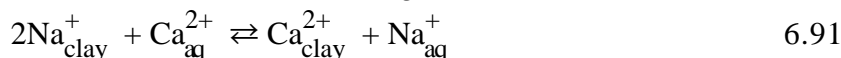
The K_d is generally applied to trace elements. Where Henry's Law holds, K_d should be independent of the concentration of the ion in solution or in the clay, but it will nevertheless depend on the overall composition of the solution and the clay (in other words, the Henry's law constant will be different for different clays and solutions).

A more general expression for the equilibrium constant is:

$$\frac{a_{Y\text{-clay}}^v}{a_{X\text{-clay}}^v} = K \frac{a_Y^v}{a_X^v} \quad 6.90$$

where v is the stoichiometric coefficient.

The power term is important. Consider the case of exchange between Na^+ and Ca^{2+} . The reaction is:



The K' expression is:

$$\frac{X_{\text{Ca}^{2+}}}{X_{\text{Na}^+}^2} = K' \frac{[\text{Ca}^{2+}]}{[\text{Na}^+]^2} \quad 6.92$$

If we assume that (1) the mole fractions of Na^+ and Ca^{2+} in the clay must sum to one (i.e., they are the only ions in the exchanging site), (2) molar concentrations in solution of 1 for Na and Ca in solution, and (3) $K' = 1$, solving equation 6.92 yields $X_{\text{Na}} = 0.62$ and $X_{\text{Ca}} = 0.38$. If we kept the ratio of Ca and Na in solution constant, but dilute their concentrations 1000 fold, we obtain $X_{\text{Na}} = 0.03$ and $X_{\text{Ca}} = 0.97$. Thus by diluting the solution, the divalent cation has almost entirely replaced the monovalent ion. The composition of the clay will thus depend on the ionic strength of the solution. The dominant exchangeable cation is Ca^{2+} in fresh water, but Na^+ in seawater.

Table 6.3. ION EXCHANGE CAPACITY OF CLAYS

Clay	Exchange Capacity (meq/100g)
Smectite	80-150
Vermiculite	120-200
Illite	10-40
Kaolinite	1-10
Chlorite	<10

MINERAL SURFACES AND THEIR INTERACTION WITH SOLUTIONS

Reactions between solutions and solids necessarily involves the interface between these phases. The details of interface processes thus govern equilibria between solids and solutions. Because clays and other sedimentary particles are typically very small, their surface area to volume ratio is high. This adds to the importance of surface chemistry. For example, the concentrations of many

CHAPTER 6: AQUATIC CHEMISTRY

trace elements, particularly the transition metals, dissolved in streams, rivers, and the oceans are controlled not by precipitation and dissolution, but rather by adsorption on and desorption from mineral and organic surfaces. These surface reactions maintain the concentrations of these elements in seawater well below saturation levels. Surface processes also play an important role in soil fertility. Soils have concentrations in soils above levels one would predict from equilibrium dissolution and precipitation because of adsorption onto particles surfaces. Surface adsorption will also strongly affect the dispersion of pollutants in soils, ground and surface waters. We discussed some aspects of surface chemistry in Chapter 5 within the context of kinetic fundamentals. We return to it in this chapter in a broader context.

Adsorption

We can define adsorption as attachment of an ion in solution to a preexisting solid surface, for example a clay particle. Adsorption involves one or more of the following:

- Surface complex formation: The formation of coordinative bonds between metals and ligands at the surface. Considered in isolation, this process is very similar to the formation of complexes between dissolved components.
- Electrostatic interactions: As we shall see, solid surfaces are typically electrically charged. This electrostatic force, which is effective over greater distances than purely chemical forces, affects surface complex formation and loosely binds other ions to the surface.
- Hydrophobic adsorption: Many organic substances, most notably lipids, are highly insoluble in water due to their non-polar nature. These substances become adsorbed to surfaces, not because they are attracted to the surface, but rather because they are repelled by water. Since hydrophobic adsorption involves organic molecules, we will deal with this topic in Chapter 14.

The interaction of the three effects make quantitative prediction of adsorption behavior more difficult than prediction of complexation in solution. The functional groups of mineral and organic surfaces have properties similar to those of their dissolved counterparts. In this sense, surface complexation reactions are similar to complexation reactions in solution. However, reactions between these surface groups and dissolved species is complicated by the proximity of surface groups to each other, making them subject to long range electrostatic forces from neighboring groups. For example, the surface charge will change systematically as the adsorbed surface concentration of a positive species such as H^+ increases. This change in surface charge will decrease the attraction between H^+ ions and the surface. As a result, the equilibrium constant for the surface protonation reaction will change as the surface concentration of H^+ increases.

We found in Chapter 5 that adsorption is usually described in terms of adsorption isotherms. We introduced two such isotherms, the Langmuir isotherm:

$$\Theta_A = \frac{K_{ad}[A]}{1 + K_{ad}[A]} \quad (5.145)$$

(where Θ_A is the fraction of surface sites occupied by species A, $[A]$ is the dissolved concentration of A, and K_{ad} is the adsorption equilibrium constant), and the Freundlich isotherm:

$$\Theta_A = K_{ad}[A]^n \quad (5.149)$$

where n is an empirical constant. We derived the Langmuir isotherm from kinetic fundamentals, though we could have also derived it from thermodynamics. Inherent in its derivation are the assumptions that (1) the free energy of adsorption is independent of the number of sites available and therefore that (2) the law of mass action applies and that (3) only a monolayer of adsorbate can form. The Langmuir isotherm thus shows a decrease in the fraction of A adsorbed when the concentration of A in solution is high, reflecting saturation of the surface. In contrast, the Freundlich isotherm, which is merely empirical, shows no saturation. We also found that at low relative saturation of the surface, the Freundlich isotherm with $n=1$ approximates the Langmuir isotherm.

Adsorption phenomena are generally treated with the *surface complexation model*, which is a generalization of the Langmuir isotherm (Stumm and Morgan, 1996; Morel and Hering, 1993). The model

CHAPTER 6: AQUATIC CHEMISTRY

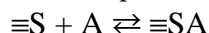
incorporates both *chemical bonding of solute species to surface atoms* and *electrostatic interactions between the surface and solute ions*. The model assumes that these two effects can be treated separately. Thus the free energy of adsorption is the sum of a complexation, or intrinsic, term and an electrostatic, or coulombic term:

$$G_{\text{ad}} = G_{\text{intr}} + G_{\text{coul}} \quad 6.93$$

From this it follows that the adsorption equilibrium constant can be written as:

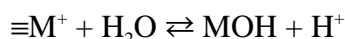
$$K_{\text{ad}} = K_{\text{intr}} K_{\text{coul}} \quad 6.94$$

Letting $\equiv S$ denote the surface site and A denote a solute species, we may write the adsorption reaction as:



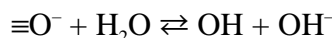
Let's begin by considering comparatively simple surfaces: those of metal oxides. Although silicates are likely to be more abundant than simple oxides, the properties of silicate surfaces approximate those of mixtures of their constituent oxides surfaces. Hence what we learn from consideration of oxides can be applied to silicates as well. We will initially focus just on the intrinsic terms in equations 6.93 and 6.94. We will return to the coulombic term at the end of this section.

Oxygen and metal atoms at an oxide surface are incompletely coordinated; i.e., they are not surrounded by oppositely charged ions as they would be in the interior of a crystal (Figure 6.29a). As a consequence, mineral surfaces immersed in water attract and bind water molecules (Figure 6.29b). These water molecules can then dissociate, leaving a hydroxyl group bound to the surface metal ion. We may write this reaction as:

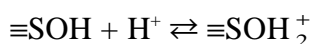


where $\equiv M$ denotes a surface metal ion.

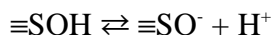
In a similar fashion, incompletely coordinated oxygens at the surface can also bind water molecules, which can then dissociate, again creating a surface hydroxyl group:



Thus the surface on an oxide immersed in water very quickly becomes covered with hydroxyl groups (Figure 6.29c), which we can write as $\equiv SOH$ and which are considered to constitute part of the surface rather than the solution. These hydroxyl groups can then act as either proton acceptors or proton donors through further association or dissociation reactions, e.g.:



or



We should not be surprised to find that these kinds of reactions are strongly pH dependent.

Adsorption of metals to the surface may occur through replacement of a surface proton, as is illustrated in Figure 6.30a, while ligands may be absorbed by replacement of a surface OH group (Figure 6.30b). The adsorbed metal may bind an additional ligand (Fig. 6.30c), and the adsorbed ligand may bind an additional metal (Fig. 6.30d).

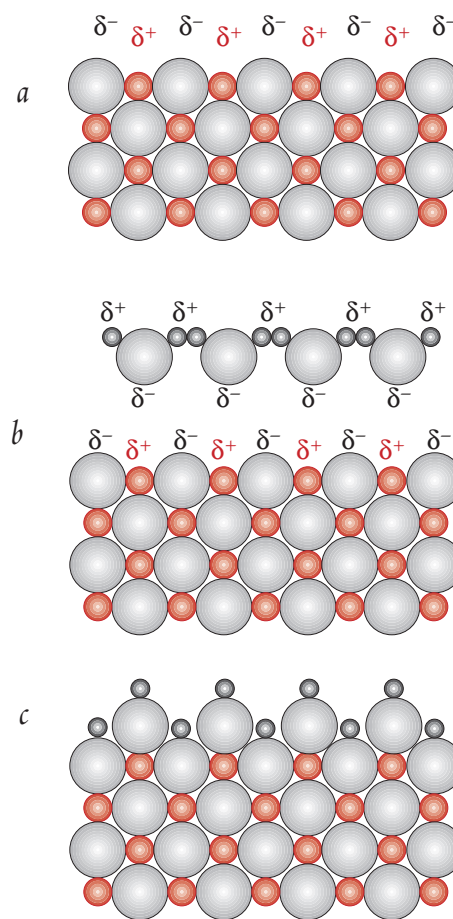
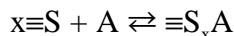


Figure 6.29. (a) Metal ions (small red spheres) and oxygens (large gray spheres) on a mineral surface are incompletely coordinated, leading to a partial charge on the surface (indicated by δ^+ and δ^-). (b) When the mineral surface is immersed in water, water molecules coordinate metal ions on the surface. (c) Water molecules will dissociate leaving hydroxyl groups coordinating metal ions. Protons (small dark spheres) will associate with surface oxygens, forming additional hydroxyl groups.

CHAPTER 6: AQUATIC CHEMISTRY

An additional possibility is multidentate adsorption, where a metal or ligand is bound to more than one surface site (Figures 6.30e and 6.30f). This raises an interesting dilemma for the Langmuir isotherm. Where x sites are involved, we could write the reaction as:



and the corresponding equilibrium constant expression as:

$$K_{ad} = \frac{[\equiv S_x A]}{[\equiv S]^x [A]} \quad 6.95$$

where x is the number of sites involved and A is the species being adsorbed. This assumes, however, that the probability of finding x sites together is proportional to the x th power of concentration, which is not the case. A better approach is to assume that the reaction occurs with a multidentate surface species, $\equiv S_x$ and that its concentration is $[\equiv S]/x$. The equilibrium constant is then:

$$K_{ad} = \frac{[\equiv S_x A]}{[\equiv S]/x [A]}$$

Alternatively, the $/x$ can be contained within the equilibrium constant.

Since surface bound protons and OH groups are almost inevitably involved in adsorption, we would expect that adsorption of metals and ligands will be strongly pH dependent. This is indeed the case, as may be seen in Figure 6.31 and 6.32: adsorption of cations increases with increasing pH while adsorption of anions decreases with decreasing pH. Figure 6.32 shows that adsorption of metals on SiO_2

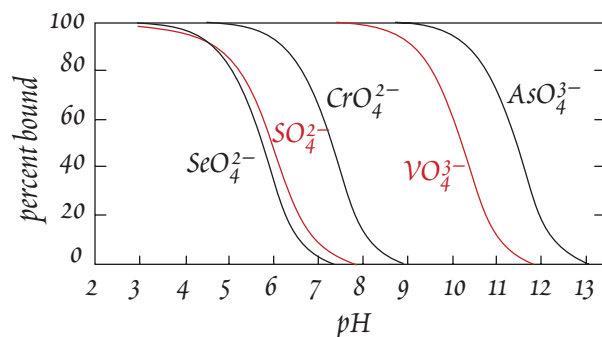


Figure 6.31. Binding of ligands (anions) on the surface of hydrous ferric oxide ($\Sigma\text{Fe} = 10^{-3} \text{ M}$) from dilution solution ($5 \times 10^{-7} \text{ M}$; $I=0.1$) as a function of pH. From Stumm and Morgan (1996).

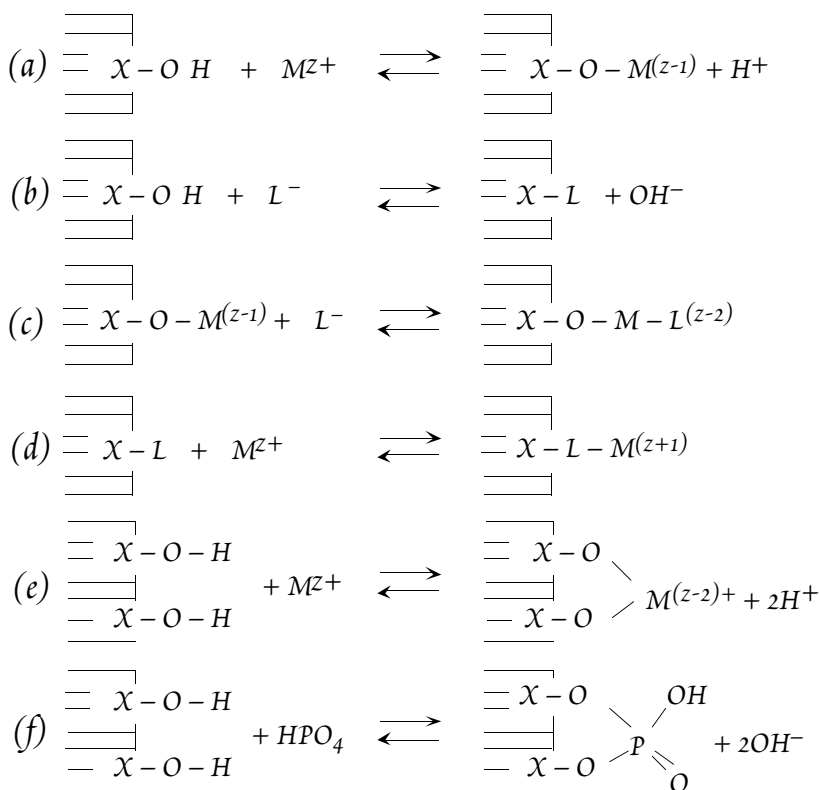


Figure 6.30. Complex formation of solid surfaces may occur when (a) a metal replaces a surface proton, or (b) a ligand replaces a surface OH group. The adsorbed metal (c) may bind an additional ligand, and the ligand (d) may bind an additional metal. Multidentate adsorption involves more than one surface site (e, f).

goes from insignificant to nearly complete over a very narrow range of pH. This strong dependence on pH certainly reflects protonation of the surface as we have discussed above, but it also reflects the extent of hydrolysis of the ion in solution.

As is the case with soluble complexes, surface complexes may be divided into inner sphere and outer sphere complexes (Figure 6.34). Inner sphere complexes involve some degree of covalent bonding between the adsorbed species and atoms on the surface. In an outer-sphere complex, one or more water molecules separate the adsorbed ion and the surface; in this case adsorption involves only electrostatic forces. The third possibility is that an ion may be held

CHAPTER 6: AQUATIC CHEMISTRY

within the diffuse layer (see following section) by long range electrostatic forces.

EXAMPLE 6.9. Adsorption of Pb²⁺ ON HYDROUS FERRIC OXIDE AS A FUNCTION OF pH

Using the following apparent equilibrium constants:



calculate the fraction of surface adsorbed Pb as a function of pH from pH 5 to pH 8 for concentrations of surface sites of 10⁻³ M, 10⁻⁴ M, and 10⁻⁵ M assuming a total Pb concentration of 10⁻⁸ M.

Answer: The quantity we wish to calculate is $[\equiv\text{FeOPb}^+]/\Sigma\text{Pb}$, so we want to find an expression for $[\equiv\text{FeOPb}^+]$ as a function of pH. We chose our components to be H⁺, Pb²⁺, and $\equiv\text{FeOH}_2^+$ and begin by writing the two relevant conservation equations:

$$\Sigma\text{Pb} = [\text{Pb}^{2+}] + [\text{PbOH}^+] + [\equiv\text{FeOPb}^+] \quad 6.98$$

$$\Sigma\equiv\text{Fe} = [\equiv\text{FeOH}_2^+] + [\equiv\text{FeOH}] + [\equiv\text{FeO}^-] + [\equiv\text{FeOPb}^+] \quad 6.99$$

From the equilibrium constant expressions, we have the following:

$$[\equiv\text{FeOH}] = \frac{[\equiv\text{FeOH}_2^+]}{[\text{H}^+]} K_{a1} \quad 6.100$$

$$[\equiv\text{FeO}^-] = \frac{[\equiv\text{FeOH}]}{[\text{H}^+]} K_{a2} = \frac{[\equiv\text{FeOH}_2^+]}{[\text{H}^+]^2} K_{a1} K_{a2} \quad 6.101$$

$$[\equiv\text{FeOPb}^+] = [\equiv\text{FeO}^-][\text{Pb}^{2+}] K_{ad}^{-1} = \frac{[\equiv\text{FeOH}_2^+]}{[\text{H}^+]^2} [\text{Pb}^{2+}] \frac{K_{a1} K_{a2}}{K_{ad}} \quad 6.102$$

Substituting equations 6.100-6.102 into 6.99 we have:

$$\Sigma\equiv\text{Fe} = [\equiv\text{FeOH}_2^+] \left\{ 1 + \frac{K_{a1}}{[\text{H}^+]} + \frac{K_{a1} K_{a2}}{[\text{H}^+]^2} + \frac{[\text{Pb}^{2+}]}{[\text{H}^+]^2} \frac{K_{a1} K_{a2}}{K_{ad}} \right\} \quad 6.103$$

Since the $[\text{Pb}^{2+}]$ is small, the last term on the right can be neglected so we have:

$$\Sigma\equiv\text{Fe} \approx [\equiv\text{FeOH}_2^+] \left\{ 1 + \frac{K_{a1}}{[\text{H}^+]} + \frac{K_{a1} K_{a2}}{[\text{H}^+]^2} \right\}$$

In a similar way, we obtain:

$$\Sigma\text{Pb} = [\text{Pb}^{2+}] \left\{ 1 + \frac{[\equiv\text{FeOH}_2^+]}{[\text{H}^+]^2} \frac{K_{a1} K_{a2}}{K_{ad}} + \frac{K_{OH}}{[\text{H}^+]} \right\}$$

Solving this pair of equations for $[\equiv\text{FeOH}_2^+]$ and $[\text{Pb}^{2+}]$, and substituting these into 6.102, we obtain:

$$[\equiv\text{FeOPb}^+] = \frac{\Sigma\equiv\text{Fe}}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}} \frac{\Sigma\text{Pb}}{1 + \frac{\Sigma\equiv\text{Fe} K_{a1} K_{a2}/K_{ad}}{[\text{H}^+]^2 + [\text{H}^+]K_{a1} + K_{a1}K_{a2}} + \frac{K_{OH}}{[\text{H}^+]}} \frac{K_{a1} K_{a2}}{K_{ad}}$$

Dividing by ΣPb and simplifying, we have:

$$\frac{[\equiv\text{FeOPb}^+]}{\Sigma\text{Pb}} = \frac{\Sigma\equiv\text{Fe} K_{a2}}{K_{ad} \left([\text{H}^+]^2/K_{a1} + [\text{H}^+] + K_{a2} \right) + ([\text{H}^+]/K_{a1} + 1 + K_{a2}/[\text{H}^+]) K_{OH} K_{ad} + \Sigma\equiv\text{Fe} K_{a2}}$$

The result is shown in Figure 6.33. For the highest concentration of surface sites, Pb goes from virtually completely insoluble to virtually completely adsorbed within 2 pH units.

CHAPTER 6: AQUATIC CHEMISTRY

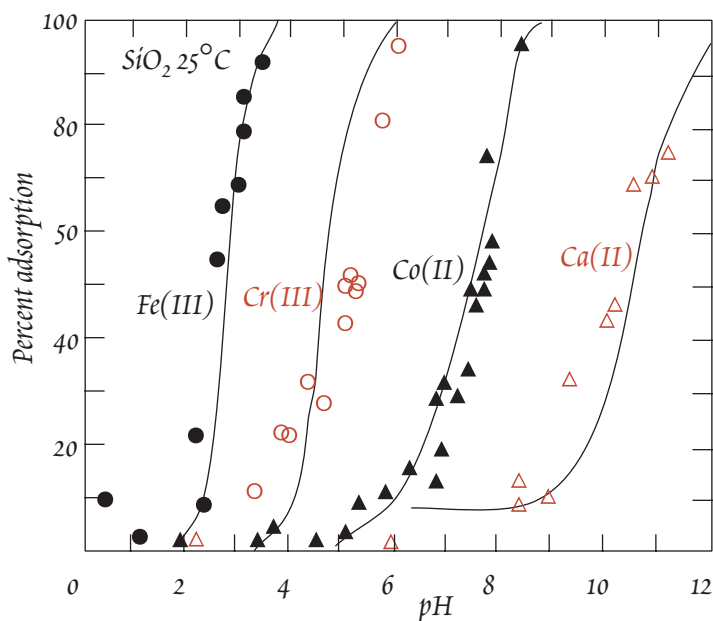


Figure 6.32. Adsorption of metals on SiO_2 . Symbols show experimentally determined values; curves show theoretical values (from James and Healy, 1972).

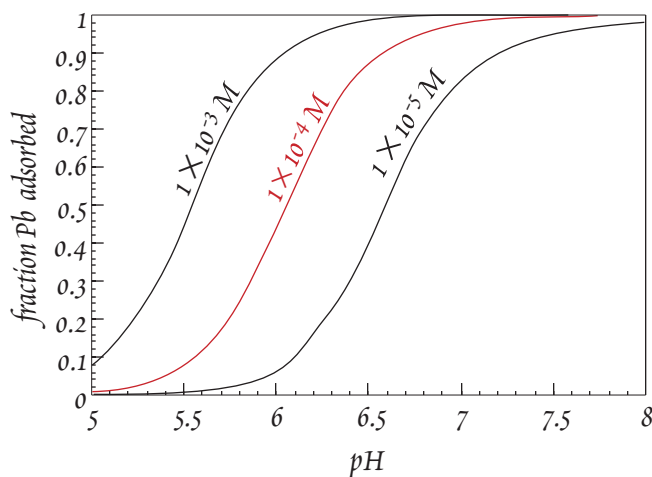


Figure 6.33. Calculated adsorption of Pb^{2+} on hydrous ferric oxide for three different concentrations of surface sites: 10^{-3} M, 10^{-4} M, and 10^{-5} M.

DEVELOPMENT OF SURFACE CHARGE AND THE ELECTRIC DOUBLE LAYER

Mineral surfaces develop electrical charge for three reasons:

1. Complexation reactions between the surface and dissolved species, such as those we discussed in the previous section. Most important among these are protonation and deprotonation. Because these reactions depend on pH, this aspect of surface charge is pH dependent. This pH dependence is illustrated in Figure 6.35.
2. Lattice imperfections at the solid surface as well as substitutions within the crystal lattice (e.g., Al^{3+} for Si^{4+}). Because the ions in interlayer sites of clays are readily exchangeable, this mechanism is particularly important in the development of surface charge in clays.
3. Hydrophobic adsorption, primarily of organic compounds, and "surfactants" in particular. We will discuss this effect in Chapter 14.

Thus there are several contributions to surface charge density. We define σ_{net} as the net density of electric charge on the solid surface, and can express it as:

$$\sigma_{\text{net}} = \sigma_0 + \sigma_{\text{H}} + \sigma_{\text{SC}} \quad 6.104$$

where σ_0 is the intrinsic surface charge due to lattice imperfections and substitutions, σ_{H} is the net proton charge, i.e., the charge due to binding H^+ and OH^- , σ_{SC} is the charge due to other surface complexes. σ is usually measured in coulombs per square meter (C/m^2). σ_{H} is given by:

$$\sigma_{\text{H}} = \mathcal{F}(\Gamma_{\text{H}} - \Gamma_{\text{OH}}) \quad 6.105$$

where \mathcal{F} is the Faraday constant and Γ_{H} and Γ_{OH} are the adsorption densities (mol/m^2) of H^+ and OH^- respectively. In a similar way, the charge due to other surface complexes is given by

$$\sigma_{\text{SC}} = \mathcal{F}(z_{\text{M}}\Gamma_{\text{M}} + z_{\text{A}}\Gamma_{\text{A}}) \quad 6.106$$

where the subscripts M and A refer to metals and anions respectively, Γ is again adsorption density and z is the charge of the ion. The surface complex term may also be broken into an inner sphere and outer sphere component:

$$\sigma_{\text{SC}} = \sigma_{\text{IS}} + \sigma_{\text{OS}} \quad 6.107$$

CHAPTER 6: AQUATIC CHEMISTRY

Thus net charge on the mineral surface is:

$$\sigma_{\text{net}} = \sigma_0 + \mathcal{F}(\Gamma_{\text{H}} - \Gamma_{\text{OH}} + Z_{\text{M}}\Gamma_{\text{M}} + Z_{\text{A}}\Gamma_{\text{A}}) \quad 6.108$$

Figure 6.35 shows that at some value of pH the surface charge will be zero. The pH at which this

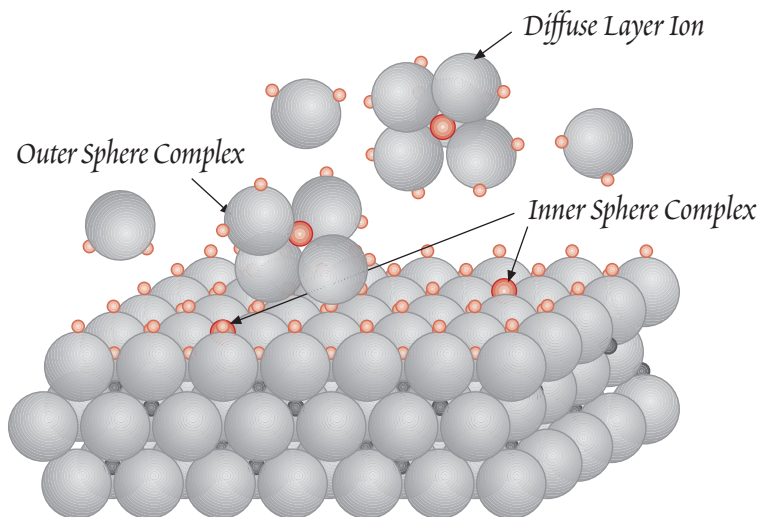


Figure 6.34. Inner sphere surface complexes involve some degree of covalent bonding between the surface and the ion; outer sphere complexes form when one or more water molecules intervenes between the surface and the ion. Ions may also be held in the diffuse layer by electrostatic forces.

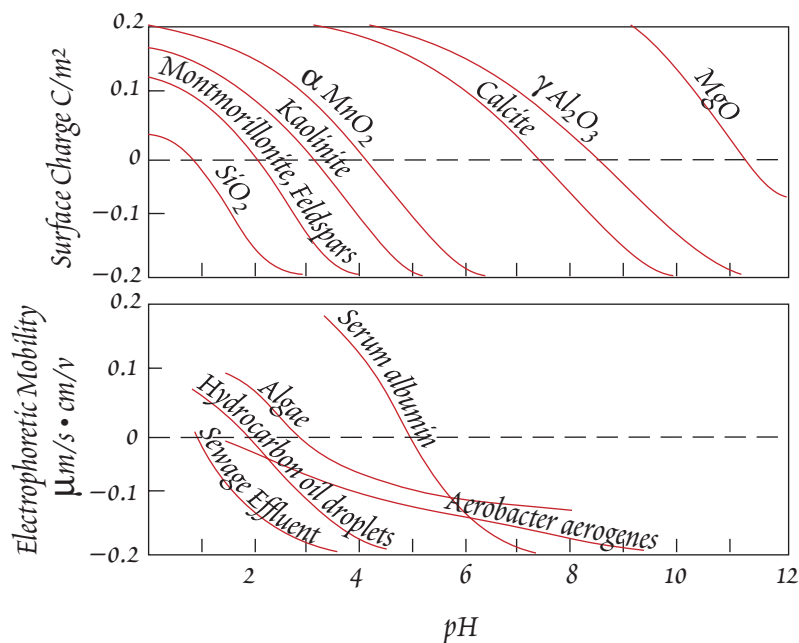


Figure 6.35. (a) Surface charge of some common sedimentary materials as a function of pH. (b) Electrophoretic mobility, which is related to surface charge, of representative organic substances as a function of pH. The pH dependence of surface charge reflects the predominance of attached protons at low pH and the predominance of attached hydroxyls at higher pH. From Stumm (1992).

occurs is known as the isoelectric point, or zero point of charge (ZPC). The ZPC is the pH at which the charge on the surface of the solid caused by binding of all ions is 0, which occurs when the charge due to adsorption of cations is balanced by charge due to adsorption of anions. A related concept is the point of zero net proton charge (pznpc), which is the point of zero charge when the charge due to the binding of H^+ and OH^- is 0; i.e., $\sigma_{\text{H}} = 0$. Table 6.4 lists values of the point of zero net proton condition for some important solids. Surface charge depends on the nature of the surface, the nature of the solution, and the ionic strength of the latter. An important feature of the point of zero charge, however, is that it is independent of ionic strength, as is illustrated in Figure 6.36.

DERIVATION OF SURFACE CHARGE

The surface charge due to binding of protons and hydroxyls is readily determined by titrating a solution containing the a suspension of the material of interest with strong acid or base. The idea is that any deficit in H^+ or OH^- in the solution is due to binding with the surface. For example consider a simple hydroxide surface with surface species $\equiv\text{SOH}_2^+$ and $\equiv\text{SO}^-$ (as well as $\equiv\text{SOH}^0$). Charge balance requires that:

$$C_{\text{A}} - C_{\text{B}} + [\text{OH}^-] + [\text{H}^+] = [\equiv\text{SOH}_2^+] - [\equiv\text{SO}^-]$$

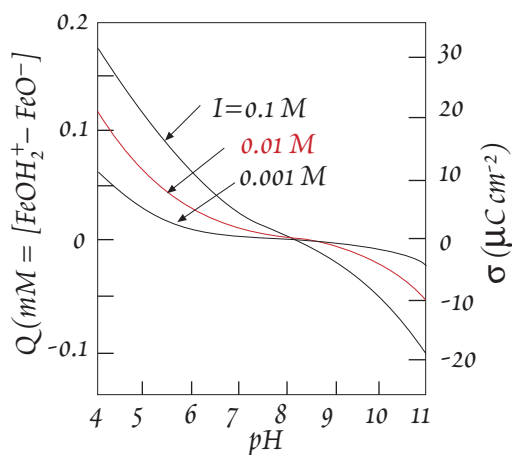
where C_{A} and C_{B} are the amount of acid or base added and $[\equiv\text{SOH}_2^+]$ and $[\equiv\text{SO}^-]$ are the concentrations (in moles per

CHAPTER 6: AQUATIC CHEMISTRY

Table 6.4. POINT OF ZERO NET PROTON CHARGE OF COMMON SEDIMENTARY PARTICLES

Material	pH
SiO ₂ (quartz)	2.0
SiO ₂ (gel)	1.0-2.5
α-Al ₂ O ₃	9.1
Al(OH) ₃ (gibbsite)	8.2
TiO ₂ (anatase)	7.2
Fe ₃ O ₄ (magnetite)	6.5
α-Fe ₂ O ₃ (hematite)	8.5
FeO(OH) (goethite)	7.8
Fe ₂ O ₃ ·nH ₂ O	8.5
δ-MnO	2.8
β-MnO	7.2
Kaolinite	4.6
Montmorillonite	2.5

From Stumm (1992).

Figure 6.36. Surface charge on FeOOH as a function of pH for different ionic strengths of a 1:1 electrolyte (10⁻³ M FeOOH). From Dzombak and Morel (1990).

reaction respectively.

SURFACE POTENTIAL AND THE DOUBLE LAYER

The charge on a surface exerts a force on ions in the adjacent solution and gives rise to an electric potential, Ψ (measured in volts), which will in turn depend on the nature and distribution of ions in solution, as well as intervening water molecules. The surface charge results in an excess concentration of oppositely charged ions (and a deficit of liked charged ions) in the immediately adjacent solution.

The surface charge and potential can be related by Gouy-Chapman Theory[‡], which is conceptually and formally similar to Debye-Hückel Theory (Chapter 3). The relationship is given by:

liter) of the surface species. The surface charge, Q (in units of moles of charge per liter), is simply:

$$Q = [\equiv\text{SOH}_2^+] - [\equiv\text{SO}^-]$$

So that the surface charge is determined from:

$$Q = C_A - C_B + [\text{H}^+] + \frac{10^{-14}}{[\text{H}^+]} \quad 6.109$$

The surface charge *density*, σ , is calculated from Q as:

$$\sigma = \frac{Q \mathcal{F}}{A [\equiv\text{S}]} \quad 6.110$$

where A is the specific surface area (m²/mol) and $[\equiv\text{S}]$ is the concentration of solid (in mols/l)^{*}.

We can write equilibrium constant expressions for the surface protonation and deprotonation reactions. For example, for surface protonation, the equilibrium constant is:

$$K = \frac{[\equiv\text{SOH}_2^+]}{[\equiv\text{SOH}][\text{H}^+]} \quad 6.111$$

At pH below the pzpc, we can consider the entire surface charge as due to $[\equiv\text{SOH}_2^+]$, so that $Q \approx [\equiv\text{SOH}_2^+]$. We may write a conservation equation for the surface as:

$$\Sigma \equiv\text{S} = [\equiv\text{SOH}_2^+] + [\equiv\text{O}^-] + [\equiv\text{SOH}^0] \quad 6.112$$

Combining equations 6.109, 6.110, 6.111 and 6.112, we have:

$$K = \frac{(\Sigma \equiv\text{S} - Q)[\text{H}^+]}{Q} \quad 6.113$$

In equation 6.109, we see that if the amount of acid (or base) added is known, the surface charge can be determined by measuring pH (from which $[\text{OH}^-]$ may also be calculated). This is illustrated in Figure 6.37.

Thus the value of the protonation reaction equilibrium constant may be calculated from the surface charge and pH. The equilibrium constant for the deprotonation reaction may be obtained in a similar way. These equilibrium constants are also known as *surface acidity constants*, and sometimes denoted (as in Example 6.8) as K_{a1} and K_{a2} for the protonation and deprotonation

^{*} If the concentration of solid is expressed in kg/l, as it commonly is, then the specific surface area should be in units of m²/kg.

CHAPTER 6: AQUATIC CHEMISTRY

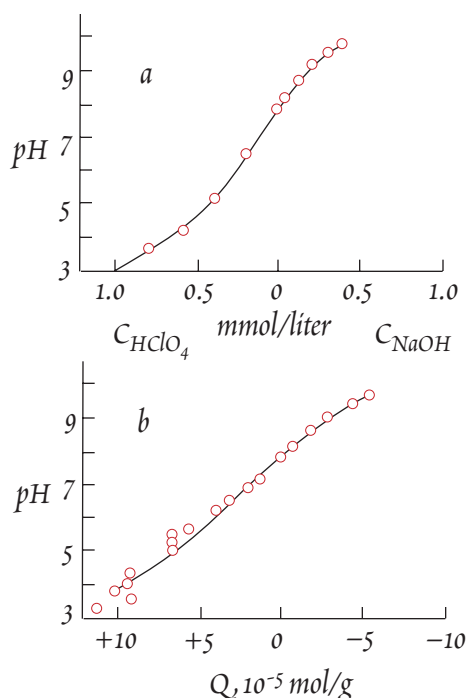


Figure 6.37. (a). Titration of a suspension of α -FeOOH (goethite) (6 g/liter) by HClO_4 and NaOH in the presence of 0.1 M NaClO_4 . (b). Charge calculated by charge balance (equation 6.c) from the titration. From Stumm (1992).

crease by $1/e$. The variation in potential, the Debye length, and the excess concentration of counterions with distance from the surface is illustrated in Figure 6.38.

An additional simplification occurs where the potential is small, namely that equation 6.114 reduces to:

$$\sigma \cong \epsilon \epsilon_0 \kappa I^{2/3} \Psi_0$$

As is illustrated in Figure 6.38, an excess concentration of oppositely charged ions develops adjacent to the surface. Thus an *electric double layer* develops adjacent to the mineral surface. The inner layer, or Stern Layer, consists of charges fixed to the surface, the outer

$$\sigma = (8 RT \epsilon \epsilon_0 I)^{1/2} \sinh\left(\frac{z \Psi_0 \mathcal{F}}{2RT}\right) \quad 6.114$$

where z is the valence of a symmetrical background electrolyte (e.g., 1 for NaCl), Ψ_0 is the potential at the surface, \mathcal{F} is the Faraday constant, T is temperature, R is the gas constant, I is ionic strength, ϵ is the permittivity of water and ϵ_0 is the permittivity of a vacuum (see Chapter 3). At 25°C , equ. 6.114 may be written as:

$$\sigma = \alpha I^{1/2} \sinh(\beta z \Psi_0)$$

where α and β are constants with value of 0.1174 and 19.5 respectively.

Where the potential is small, the potential as a function of distance from the surface is:

$$\Psi(x) = \Psi_0 e^{-\kappa x} \quad 6.115$$

where κ has units of inverse length and is called the Debye parameter or Debye length and is given by:

$$\kappa = \sqrt{\frac{2 \mathcal{F}^2 I}{\epsilon \epsilon_0 RT}} \quad 6.116$$

From equation 6.115, we see that the inverse of κ is the distance at which the electrostatic potential will de-

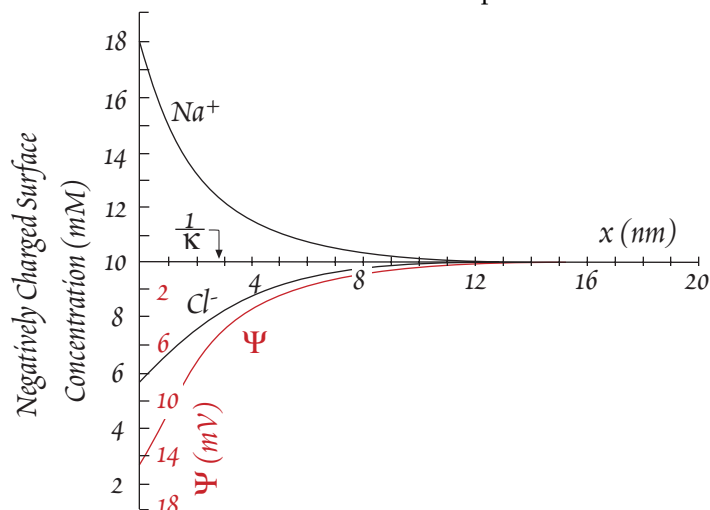


Figure 6.38. Variation in electrical potential and ions with distance from a negatively charged surface based on the Gouy-Chapman model. Electrical potential varies exponentially with distance, as do ion concentrations. $1/\kappa$ is the distance where the potential has decreased by $1/e$. From Morel and Hering (1993).

[‡] Gouy and Chapman Theory assumes an infinite flat charge plane in one dimension. The electrostatic interaction between the surface and a cloud of charged particles is described by the Poisson-Boltzmann equation, as in Debye-Hückel Theory. Unlike Debye-Hückel, the Poisson-Boltzmann equation has an exact case. The theory was developed by Gouy and Chapman around 1910, a decade before Debye and Hückel developed their theory. See Morel and Hering (1993) for the details of the derivation.

CHAPTER 6: AQUATIC CHEMISTRY

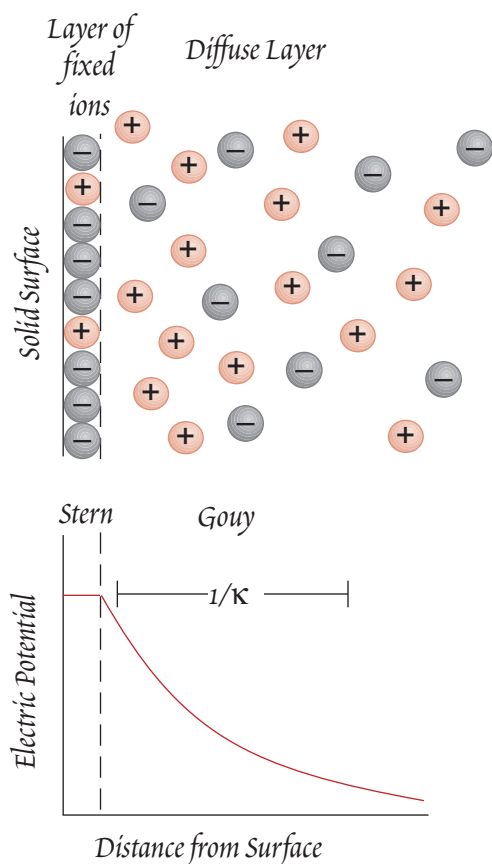


Figure 6.39. The double layer surrounding clay particles.

diffuse layer, or Gouy Layer, consists of dissolved ions that retain some freedom of thermal movement. This is illustrated in Figure 6.39. The Stern Layer is sometimes further subdivided into an inner layer of specifically adsorbed ions (inner sphere complexes) and an outer layer of ions that retain their solvation shell (outer sphere complexes), called the inner and outer Helmholtz planes respectively. Hydrogens adsorbed to the surface are generally considered to be part of the solid rather than the Stern Layer. The thickness of the Gouy (outer) Layer is considered to be the Debye length, $1/\kappa$. As is apparent in equation 6.116, this thickness will vary inversely with the square of ionic strength. Thus the Gouy Layer will collapse in high ionic strength solutions and expand in low ionic strength ones.

When clays are strongly compacted, the Gouy layers of individual particles overlap and ions are virtually excluded from the pore space. This results in retardation of diffusion of ions, but not of water. As a result, clays can act as *semi-permeable membranes*. Because some ions will diffuse easier than others, a chemical fractionation of the diffusing fluid can result.

At low ionic strength, the charged layer surrounding a particle can be strong enough to repel similar particles with their associated Gouy layers. This will prevent particles from approaching closely and hence prevent coagulation. Instead, the particles form a relatively stable *colloidal* suspension. As the ionic strength of the solution increases, the Gouy layer is compressed and the repulsion between particles decreases. This allows particles to approach closely enough that they are bound together by attractive van der Waals forces between them.

When this happens, they form larger aggregates and settle out of the solution. For this reason, clay particles suspended in river water will flocculate and settle out when river water mixes with seawater in an estuary.

EFFECT OF THE SURFACE POTENTIAL ON ADSORPTION

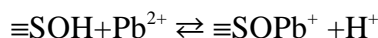
The electrostatic forces also affect complexation reactions at the surface, as we noted at the beginning of this section. An ion must overcome the electrostatic forces associated with the electric double layer before it can participate in surface reactions. We can account for this effect by including it in the Gibbs Free Energy of reaction term, as in equation 6.93:

$$G_{\text{ads}} = G_{\text{intr}} + G_{\text{coul}} \quad (6.93)$$

where ΔG_{ads} is the total free energy of the adsorption reaction, ΔG_{intr} is the *intrinsic* free energy of the reaction (i.e., the value the reaction would have in the absence of electrostatic forces; in general this will be similar to the free energy of the same reaction taking place in solution), and ΔG_{coul} is the free energy due to the electrostatic forces and is given by:

$$G_{\text{coul}} = \mathcal{F} Z \Psi_0 \quad 6.121$$

where ΔZ is the the change in molar charge of the surface species due to the adsorption reaction. For example, in the reaction:



CHAPTER 6: AQUATIC CHEMISTRY

The value of ΔZ is +1 and $\Delta G_{\text{coul}} = \mathcal{F}\Psi$.

Thus if we can calculate ΔG_{coul} , this term can be added to the intrinsic ΔG for the adsorption reaction (ΔG_{intr}) to obtain the effective value of ΔG (ΔG_{ads}). From ΔG_{ads} it is a simple and straightforward matter to calculate K_{ads} . From equation 3.98 we have:

EXAMPLE 6.10. EFFECT OF SURFACE POTENTIAL ON SURFACE SPECIATION OF FERRIC OXIDE

Using the surface acidity constants given in Example 6.9, calculate the surface speciation of hydrous ferric oxide as a function of pH in a solution with a background electrolyte concentration of $I = 0.1$ M. Assume the concentration of solid is 10^{-3} mol/l, the specific surface area is 5.4×10^4 m²/mol and that there are 0.2 mol of active sites per mole of solid.

Answer: The concentration of surface sites, $\Sigma \equiv \text{Fe}$, is 0.2 mol sites/mol solid $\times 10^{-3}$ mol solid/l = 2×10^{-4} mol sites/l. Our conservation equation is:

$$\Sigma \equiv \text{Fe} = [\equiv \text{FeOH}_2^+] + [\equiv \text{FeOH}] + [\equiv \text{FeO}^-] = 2 \times 10^{-4}$$

We define P as:

$$P = e^{-\mathcal{F}\Delta Z\Psi_0/RT} \quad 6.117$$

so that our equilibrium constant expressions (12.96 and 12.97) become:

$$[\text{FeOH}] = \frac{[\text{FeOH}_2^+]}{[\text{H}^+]} K_{a1} P^{-1} \quad 6.118$$

and

$$[\text{FeO}^-] = \frac{[\text{FeOH}]}{[\text{H}^+]} K_{a2} P^{-1} = \frac{[\text{FeOH}_2^+]}{[\text{H}^+]^2} K_{a1} K_{a2} P^{-2} \quad 6.119$$

Substituting into our conservation equation, and solving for $[\equiv \text{FeOH}_2^+]$ we have:

$$[\text{FeOH}_2^+] = \Sigma \equiv \text{Fe} \left\{ 1 + \frac{K_{a1} P^{-1}}{[\text{H}^+]} + \frac{K_{a1} K_{a2} P^{-2}}{[\text{H}^+]^2} \right\}^{-1} \quad 6.120$$

The concentration of surface charge, Q , is simply:

$$Q = [\equiv \text{FeOH}_2^+] - [\equiv \text{FeO}^-]$$

and the surface charge density is:

$$\sigma = \frac{\mathcal{F}}{A S} ([\text{FeOH}_2^+] - [\text{FeO}^-])$$

(P enters the equations as the inverse because we have defined the equilibrium constants in Example 6.9 for the *desorption* reactions.) Substituting into the surface charge density equation, we have:

$$\sigma = \frac{\mathcal{F}}{A S} [\text{FeOH}_2^+] \left\{ 1 - \frac{K_{a1} K_{a2} P^{-2}}{[\text{H}^+]^2} \right\}$$

Substituting equation 6.118 into this, we have:

$$\sigma = \frac{\mathcal{F}}{A S} \Sigma \equiv \text{Fe} \left\{ 1 + \frac{K_{a1} P^{-1}}{[\text{H}^+]} + \frac{K_{a1} K_{a2} P^{-2}}{[\text{H}^+]^2} \right\}^{-1} \left\{ 1 - \frac{K_{a1} K_{a2} P^{-2}}{[\text{H}^+]^2} \right\}$$

Finally, substituting equation 6.114 for σ , and 6.117 for P , we have:

$$\sinh(\beta z \Psi_0) = \frac{\mathcal{F}}{A S \alpha I^{1/2}} \Sigma \equiv \text{Fe} \frac{1 - \frac{K_{a1} K_{a2} e^{2\mathcal{F}\Delta Z\Psi_0/RT}}{[\text{H}^+]^2}}{1 + \frac{K_{a1} e^{\mathcal{F}\Delta Z\Psi_0/RT}}{[\text{H}^+]} + \frac{K_{a1} K_{a2} e^{2\mathcal{F}\Delta Z\Psi_0/RT}}{[\text{H}^+]^2}}$$

A pretty intimidating equation, and one with no direct solution. It can, however, be solved by indirect methods (i.e., iteratively) on a computer. A quick and easy way is to use the Solver feature in Microsoft ExcelTM. Figure 6.40 shows the results and compares them to the surface speciation when surface potential is not considered. The effect of including the surface potential term is reduce the surface concentration of $\equiv \text{FeO}^-$ and $\equiv \text{FeOH}_2^+$ and broaden the pH region where $\equiv \text{FeO}$ dominates.

CHAPTER 6: AQUATIC CHEMISTRY

$$K = e^{-\Delta G_{\text{ads}}/RT}$$

substituting equation 6.94, we have:

$$K = e^{-\Delta G_{\text{intr}}/RT} e^{-\Delta G_{\text{coul}}/RT} \quad 6.122$$

Since $K_{\text{intr}} = e^{\Delta G_{\text{intr}}/RT}$ and $\Delta G_{\text{coul}} = \mathcal{F}\Delta Z\Psi_0$, we have:

$$K = K_{\text{intr}} e^{-\mathcal{F}\Delta Z\Psi_0/RT} \quad 6.123$$

Thus we need only find the value of Ψ_0 , which we can calculate from σ using equation 6.114. Example 6.10 illustrates the procedure.

The effect of surface potential on a given adsorbate will be to shift the adsorption curves to higher pH for cations and to lower pH for anions. Figure 6.41 illustrates the example of adsorption of Pb on hydrous ferric oxide. When surface potential is considered, adsorption of a given fraction of Pb occurs at roughly 1 pH unit higher than in the case where surface potential is not considered. In addition, the adsorption curves become steeper.

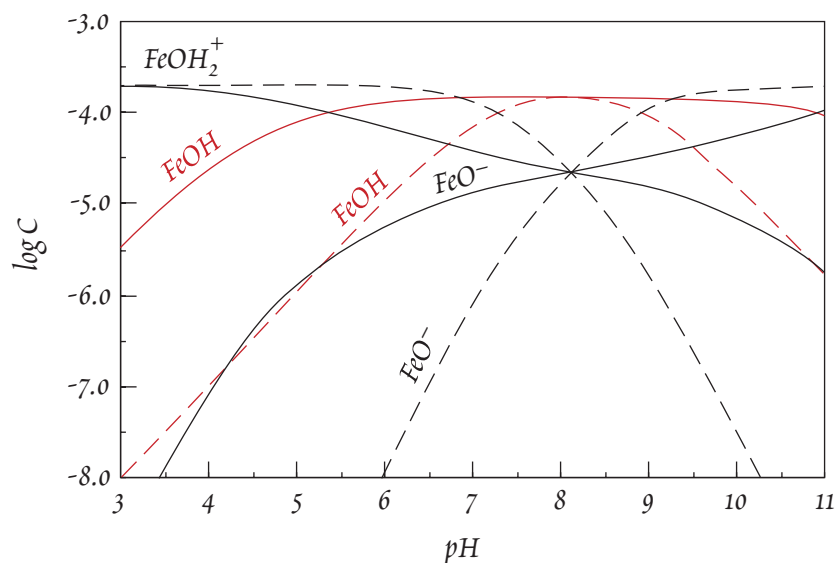


Figure 6.40. Surface speciation of hydrous ferric oxide for $I = 0.1$ M calculated in Example 6.9. Solid lines show speciation when surface potential term is included, dashed lines show the calculated speciation with no surface potential.

REFERENCES AND SUGGESTIONS FOR FURTHER READING

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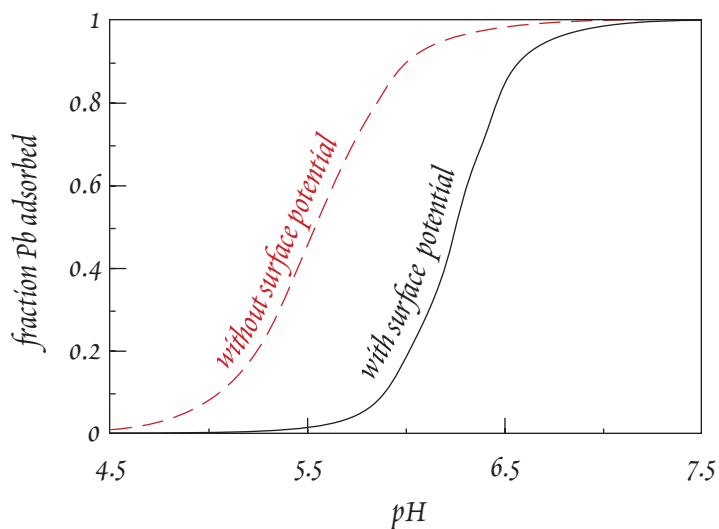


Figure 6.41. Comparison of calculated adsorption of Pb on hydrous ferric oxide with and without including the effect of surface potential.

CHAPTER 6: AQUATIC CHEMISTRY

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PROBLEMS

- Using the composition given in Problem 3.4, calculate the alkalinity of seawater at 25°C.
- For a sodium carbonate solution titrated with HCl to the bicarbonate equivalence point, show that:

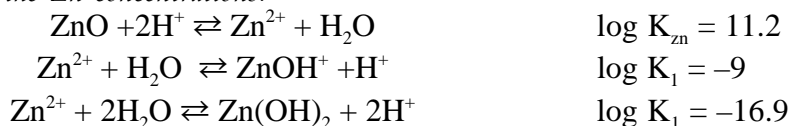
$$\Sigma\text{CO}_2 = [\text{Cl}^-] + [\text{OH}^+]$$

- Calculate the pH of a solution containing $\Sigma\text{CO}_2 = 10^{-2}$ at 25°C at the bicarbonate and carbonate equivalence points. Use the equilibrium constants in Table 6.1.

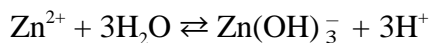
- Consider a 0.005M solution of Na_2CO_3 at 25°C.
 - What is the pH of this solution?
 - What is the pH of this solution when titrated to the bicarbonate equivalence point?
 - What is the pH of this solution when titrated to the CO_2 equivalence point?
- Consider a 0.01M solution of NaHCO_3 (sodium bicarbonate) at 20°C.
 - What is the pH of this solution?
 - Plot the titration curve for this solution (i.e., moles of HCl added vs. pH).
 - What is the pH of the CO_2 equivalence point of this solution?
- Explain why pH changes rapidly near the bicarbonate and CO_2 equivalence points during titration.
- Calculate the buffer capacity of a solution initially in equilibrium with calcite for pH between 6 and 9 at 25°C.
- Calculate the calcium ion concentration for a solution in equilibrium with calcite and fixed ΣCO_2 of 10^{-2} M at 25°C.

- Show that the α , fraction of copper complexed as CuOH^+ as defined in 6.48, will decrease with increasing concentration copper in solution. Assume ideal behavior and that H^+ , OH^- , Cu^+ and CuOH^+ are the only ions present in solution and that the stability constant of CuOH^+ is 10^{-8} .

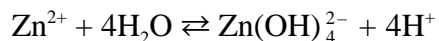
- Using the following equilibrium constants and reactions, make a plot of Zn^{2+} , ZnOH^+ , Zn(OH)_2 , Zn(OH)_3^- , Zn(OH)_4^{2-} , and total zinc concentration as a function of pH from pH 1 to pH 14. Assume ideal behavior and that H^+ , OH^- , and various species of Zn are the only ions in solution. *Hint: Use a log scale for the Zn concentrations.*



CHAPTER 6: AQUATIC CHEMISTRY

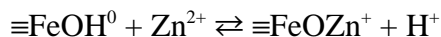


$$\log K_1 = -28.1$$



$$\log K_1 = -40.2$$

11. For the adsorption of Zn^{2+} on hydrous ferric oxide:



the apparent equilibrium constant is $10^{0.99}$. For this problem, use the surface acidity constants (i.e., equilibrium constants for adsorption and desorption of H^+) given in equations 6.96 and 6.97 (Example 6.9).

- Make a plot of Θ_{Zn} (fraction of sites occupied by Zn) vs. the aqueous concentration of Zn^{2+} at pH 7 and a total concentration of surface sites of 10^{-3} M. Assume that Zn^{2+} forms no complexes in solution.
- Ignoring electrostatic effects and any aqueous complexation of Zn^{2+} , make a plot of the fraction of Zn^{2+} adsorbed as a function of pH (beginning at pH 6), assuming a total Zn^{2+} concentration of 10^{-8} M.
- Do the same calculation as in b, but take into consideration the aqueous complexation reactions and equilibrium constants in Problem 10.